RESPONSE OF E-GLASS/EPOXY COMPOSITE TO UP AND DOWN-THERMAL SHOCKS UNDER THE INFLUENCE OF VARYING ENVIRONMENTAL CONDITION

Thesis submitted in partial fulfillment of the requirement
For the award of the degree of

Master of Technology (Research)
in

METALLURGICAL AND MATERIALS ENGINEERING

By

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Dedicated

To

My Parents

&

Family

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CERTIFICATE

*This is to certify that the thesis entitled, "**Response of E-Glass/Epoxy Composite to Up and Down-Thermal Shocks under the Influence of Varying Environmental Condition**" submitted by Mr. Ananta Prasad Chakraverty in partial fulfillment of the requirements for the award of Master of Technology (Research) Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University), is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.*

Prof. U.K. Mohanty
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Date:

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NIT, ROURKELA *Ananta Prasad Chakraverty*

CONTENTS

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ABSTRACT

The glass fiber reinforced epoxy composites, like any other fiber reinforced polymer composites, offer many advantages over the conventional structural materials. These materials have good corrosion resistance, good toughness, good insulation property and high specific strength. These properties have encouraged their use in several Civil Engineering applications, Aerospace Engineering, Transport and Marine Engineering. However, these materials suffer from significant moisture absorption properties, moisture coming from both the ambience and direct immersion in ordinary/sea water during the course of their use. The absorbed moisture causes high residual stresses while badly affecting the structural integrity of the composite. The quantity of moisture absorbed and its effect on the composite component in any engineering applications is also greatly influenced by the temperature fluctuations. Thus to ensure the effective and safe use of these materials in various fields of application, it is imperative that these materials be evaluated under the exposure to the ambience as well as temperature fluctuations.

Keeping the above in mind the present work aims at evaluating the glass fiber-epoxy composite under various exposures. The eighteen-layered glass fiber-epoxy composite fabricated in the laboratory is exposed to hydroscopic, hygroscopic and seawater environment coupled with up-thermal and down-thermal shocks for various lengths of time. Their Inter laminar shear strength (ILSS) is determined using INSTRON. The glass transition temperature (T_g) is determined using low temperature DSC. The mode of failure is

analyzed through several micrographs as obtained by inspecting the broken surface using the SEM technique.

The results establish that moisture ingression into the composite body is partly conducted by diffusion involving transport of water molecules into the matrix and in some cases into the fiber; longer exposures to moisture causing greater degradation of the composite assisting further moisture uptake by way of delaying the saturation level of moisture in the composite body. The ILSS of the composites with different exposures show different trends. While a longer hydroscopic exposure actually shows an increase in the ILSS after initial low values, the hygroscopic exposure reveals a fluctuation in the ILSS value. Exposure to seawater does not affect the ILSS much initially. However, a prolonged exposure to seawater shows a sudden decrease in the ILSS value. The ILSS is seen to vary differently with up & down thermal shocks when exposed to different ambient conditions. Lowest T_g is recorded for samples with hygroscopic exposure under up-thermal shock. Compared to all the other cases seawater exposure is seen to lower the T_g considerably, the decrease in T_g reflecting a lowering trend in the ILSS value. The SEM micrographs reveal the failure modes such as fiber fragmentations, de-laminations, fiber pull-out, fiber-matrix de-bonding etc.

KEY WORDS: Glass fibre-Epoxy Composites, Inter Laminar Shear Stress, Thermal Shock, Fibre Fragmentation, Glass Transition Temperature

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Chapter-1

INTRODUCTION

1. INTRODUCTION

It has been a challenging job to find materials to perform under given environmental conditions and for this the researchers have been contributing significantly over the years. The concept of the creation of new materials with distinguished properties is the mother of conception of creating composite materials. This very concept is responsible for creating composite materials of various types with a matrix that is strengthened by the reinforcement it contains. It is needless to say, neither the matrix nor the reinforcement can singularly possess the characteristic resulting properties of the composite, of which they are the constituents and that the composite can be tailor-made to perform in varying ambient conditions satisfactorily by adopting different processes for fabrication using varying proportions of the matrix and the reinforcement and even by changing either type of the matrix or the reinforcement or both of them.

Now-a-days polymer matrix composites (PMCs) have emerged as a class of material capable of advanced structural, aerospace engineering and marine engineering applications. Due to qualities such as versatility, low cost and light weight, polymers are increasingly used in many industries to substitute some conventional materials and alloys. PMCs offer some good characteristics such as low density, high specific strength, good anticorrosion properties, fatigue resistance and low manufacturing costs.

The fibrous polymeric composites depending on the type of nature of the fiber constitution constitute an important branch in modern engineering materials. The potential advantages of polymer matrix composites play an important role when glass fibers of different type come into existence. Today glass fiber reinforced plastic (GFRP) composites are high volume commodity materials. New markets of GFRPs in both transportation and infrastructure applications promise to accelerate the demand for glass fibers well into the twenty first century. With the increasing applications of glass fiber reinforced polymer matrices, more and more knowledge is needed to get a better understanding of the materials

which can lead to different mechanical properties of the materials. Today over 95% of commercial glass fiber reinforcing agents are made from E-type compositions.

The most important polymer matrix for fabrication of GFRP is Epoxy resin. Epoxy resin is relatively low molecular weight pre polymers capable of being processed under variety of conditions. Epoxy resin can be partially cured and stored in that state. It can exhibit low shrinkage during curing which is the main advantage over unsaturated polyster resin.

Environmental agents that may cause damage to composites are electromagnetic effects, fire and high temperature, lightning and electrical discharges, chemical degradation, ultraviolet radiation, out-gassing at high vacuum, erosion by rain and sand, moisture uptake and contact with organic liquids such as fuels, lubricants and deicing fluids. FRP structures can work in more or less aggressive environments i.e. temperature, humidity, corrosive environments, chemical exposition. Their sensitivity to the different environments parameters must be taken into account before putting them into service. In particular, when the humidity and the temperature act at the same time, they represent a danger to the long term stability of these structures. Temperature variation and humidity absorption cause an irreversible hygrothermal deterioration of the material. Environmental exposure coupled with moisture and thermal shock most often leads to matrix degradation, fiber/matrix de-bonding and delamination in polymer composites. The use of composite in safety critical applications leads to uneasiness since the mechanical response is not well understood in active and complex environmental condition like moisture at ambience as well as at elevated. The nature and order of degradation by such complex and active environment need to be critically investigated to expand the acceptability of such type of PMCs like E-glass/epoxy composites.

It is now well known that the exposure of polymeric composites in moist environments, under both normal and sub-zero conditions, leads to certain degradation of its mechanical properties which necessitates proper understanding of the correlation between the moist environment and the structural integrity. The deterioration that occurs is FRP during the service life is in general, linked to the level of moisture that is absorbed.

The absorption of moisture can be attributed largely to the affinity for moisture of specific functional groups of a highly polar nature in the cured epoxy resin. The absorption of moisture causes plasticization of the resin to occur with a concurrent swelling and lowering the glass transition temperature of the resin. This adversely affects the fiber matrix adhesion properties, resulting debonding at fiber/matrix interfaces, micro-cracking in the matrix, fiber fragmentations, continuous cracks and several other phenomena that actually degrades the mechanical property of the composites. Plasticization induces plastic deformation in addition to lowering of glass transition temperature. Swelling is related to the differential strain which is created by the expansion force exerted by the liquid while stretching the polymeric chain. The presence of moisture and the stress associated with moisture induce dilatational expansion may cause damage tolerance and structural durability.

FRP structures come across with the several of thermal environments; when they are exposed to use in day to day life. Again thermal expansion coefficients of polymers are substantially greater compared to metals and ceramics. This is why failure of the bond between fiber and resin occurs under the influence of temperature gradient. Thermal stresses caused by temperature gradient should be given special attention in many application areas.

It is in this context that the present investigation has been taken up to evaluate the desirable as well as detrimental effect of different moist environments coupled with thermal shocks on E-Glass/Epoxy laminated composites. The eighteen-layered glass fiber/epoxy composites are fabricated by adopting hand lay-up method in the laboratory. The layered based composites are exposed to hydroscopic, hygroscopic and seawater environment coupled with up-thermal and down-thermal shocks for various lengths of time. Their Inter laminar shear strength (ILSS) is determined using INSTRON-1195 with low crosshead velocity. The glass transition temperature (T_g) is determined using low temperature DSC. The mode of failure is analyzed through several micrographs as obtained by investigating the broken surface using the SEM technique.

This report contains six numbers of distinct chapters. The 1st chapter, ‘Introduction’ attempts to give an insight to the work under taken and high lights the procedure adopted in the completion of the investigation.

The 2nd chapter on 'Literature Survey' is dedicated to an extensive survey of the work carried out by other investigators/agencies in the field. The help of work carried out by these workers has been referred to wherever necessary to explain and support the present experimental findings. This chapter includes some conclusive findings from different literatures, which are listed in a tabular form.

The 3rd chapter, 'Experimental Design' is devoted to explain the experimental procedure adopted in the present investigation along with the experimental arrangements and details of experiments carried out. The instruments/apparatus and the prescribed experimental norms as adopted in the present investigations have been explained in details.

The 4th chapter houses the results in the form of tables, graphs, bar-diagrams, SEM – micrographs etc. which have been generated while carrying out the investigations. This also houses a detailed discussion of the results made on the basis of the experimental data.

On the basis of the experimental findings some useful conclusions have been provided in the 5th chapter. Finally, the references of the literatures are listed in the 6th and the last chapter.

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Chapter-2

LITERATURE SURVEY

LITERATURE SURVEY

LITERATURE SURVEY

2.1 INTRODUCTION

There has been a tremendous achievement in the science and technology of composite material in recent times [1]. These materials have greatly improved since the 1970's and their use has expanded rapidly in the world of industry. Their contribution is essential to different leading industry sectors. They are used because of their low mass and exceptional performance [2]. Many composites used today are at the leading edge of materials technology with performance and costs justifying their ultra demanding applications.

A composite is a structural material that consists of two or more combined constituents which are not soluble in each other. One constituent is called the reinforcing phase and the one in which it is embedded is called the matrix. The reinforcing phase material may be in the form of fibers, particles or flakes. The matrix phase material is generally continuous. Examples of composite system include concrete reinforced with steel and epoxy reinforced with graphite fibers [3]. Wood with lignin matrix reinforced with cellulose fibers and bones and teeth with matrix of tough organic constituent called collagen reinforced with hydroxy apatite or osteones are the common examples of natural composites combining two or more material together [4]. To make a composite is more work than just using traditional monolithic metals such as steel and aluminium [3].

Composite materials offer a number of potential advantages in various applications like aerospace applications, ship building industry, automotive, civil application due to the distinct advantages over many conventional materials like aluminium and steel. The major benefit is their low density, excellent durations, higher specific strength and stiffness, superior corrosion resistance, improved fatigue properties, life cycle cost reduction, design flexibility [5, 6]. Undoubtedly, the most important drawback is their susceptibility to out-of-plane impact damage such as that imparted by the accidental fall of a tool. Often repair procedures are utilized to provide a solution to the impact damage

problem; however they are time consuming and present certain practical difficulties especially if they are applied in the real field of applications [6]. The matrix phase of composites binds the fibers together and acts as the medium by which an extremely applied stress is transmitted and distributed to the fibers; only a very small proportion of an applied load is sustained by the matrix phase. Furthermore, the matrix material should be ductile. In addition; the elastic modulus of the fiber should be much higher than that of the matrix. The matrix also protects individual fibers from the surface damage as a result of mechanical abrasion or chemical reactions with environment.

The three main classes of composites according to the nature of matrix are (i) Metal Matrix Composite (MMC) (ii) Polymer Matrix Composite (PMC) (iii) Ceramic Matrix Composite (CMC). More recently, there has been considerable interest in Metal Matrix Composites (MMCs) such as aluminium reinforced with ceramic particles or short fibers and titanium containing long, large diameter fibers. The property enhancement being sought by the introduction of reinforcement are often less pronounced than for polymers with improvement in high temperature performance or tribological properties often of interest while various industrial applications have been developed or are being explored for MMCs [4].

Metal Matrix Composites, alternatives to conventional materials, provide the specific mechanical properties necessary for elevated as well as ambient temperature applications. The performance advantages of these materials include their tailored mechanical, physical and thermal properties in light of their low density, high specific modulus, high strength, high thermal conductivity, good fatigue response, control of thermal expansion, high abrasion and wear resistance, etc. Some of the typical applications of MMCs include their use in fabrication of satellite, missile, helicopter structures, structural support, piston, sleeves and rims, high temperature structures, drive shaft, brake rotors, connecting rods, engine block liners various types of aerospace and automotive applications etc [7]. Aluminium alloy reinforced with SiCp mainly used in automotive industry [8].

In PMCs the polymers are used as matrix materials in the greatest diversity of composite applications, as well as the largest quantities in light of their properties and ease of fabrication. Common matrix polymers include nearly all commercial thermoplastic and thermosetting polymers [9]. In ceramic Matrix composites (CMCs) the objective is usually to impart toughness to the matrix by introduction of other constituents since the stiffness and strength are unlikely to be much affected. Such materials are still for the most part, in the early stages of development partly because they are rather difficult to manufacture. In considering the formulation of a composite material for a particular type of applications, it is important to consider the properties like stiffness, strength and toughness exhibited by the potential constituents [4].

2.1.1 POLYMER MATRIX COMPOSITE:

Polymer Matrix composites (PMCs) are to date the most successful composite material system with a wide range of applications spanning from electronic products such as printed circuit board to advanced aerospace structures such as in reusable launch vehicles. This is mainly due to the variety of properties that can be achieved by combining fibers of glass, carbon, aramid and polythene together with mixtures of these using thermosetting or thermoplastic polymers as matrix materials. The fiber configuration or architecture (short, long, straight, woven, braided, laminated etc.) and the fiber surface treatment for the desired interface characteristics determine the final properties and the composite durability. Furthermore, PMCs can be combined with metals and ceramics in a variety of ways to produce special purpose products [10].

The processing of polymer matrix composites (PMCs) need not involve high pressures and does not require high temperatures. It follows that problems associated with the degradation of the reinforcement during manufacture are less significant for PMCs than for composites with other matrices. Also the equipments required for PMCs may be simpler. For these reasons polymer matrix composites developed rapidly and soon become accepted for structural applications. Today glass-reinforced polymers are still by far the most used composites material in terms of volume with the exception of concrete [11]

The PMCs properties are strongly dependent on the factors such as the matrix and fiber material and their volume fractions, the fiber orientation, the applied stress levels and strain rates as well as the loading conditions and the nature of the fiber polymer interface. The local response of the fiber matrix interface within the composite plays an important role in determining the gross mechanical performances. It provides a means of stress transfer from fiber to fiber through the matrix. In cold condition, high residual stresses can build up within the fibrous composite materials due to different coefficients of thermal expansion of the fiber and the matrix and at low temperature the polymer matrix experiences embrittlement which can also affects the properties of the composite [12]. Due to qualities such as versatility, low cost and light weight, polymers are increasingly used in many industries to substitute metals and ceramics. A wise choice of a suitable resin with the right mix of additives, filler and reinforcements allows the production of materials with remarkable properties, useful in a number of different fields of applications. If on one hand formulation is strength of polymeric materials because it confers a significant versatility, on the other hand it leads to a wide range of components that, if not blended in on optimal way, easily bring about failures and defects [13].

2.1.2 APPLICATIONS OF PMCs :

Now-a-days polymer matrix composites are in massive demand for applications in the field of aerospace vehicles, automobile parts, satellites, sports goods, robots and thermal insulation structures like cryostats for low temperature technology, hydrogen technology tanks in superconductivity and also in biomedicine for body compatible implants. These materials exhibit exceptionally good characteristics such as low density, high specific strength, good anticorrosion properties, fatigue resistance and low manufacturing costs. These materials have received increased attention for applications in cryogenic environment. Recently one area identified as potential source for significant weight reduction in the replacement of traditional metallic cryogenic fuel tanks with advanced polymeric matrix composites (PMC) tanks [14]. Fibers reinforced plastic (FRP) plates, symmetrically as well as asymmetrically laminated, are widely employed in a variety of industrial applications. For no structural applications, chopped strands mats and woven fabrics are usually used for reinforcing such plates [15]. The

mechanical properties of fiber-reinforced composites are dependent on factors such as fiber type and quantity, the adhesion between matrix and fibers, the polymerization shrinkage of the resin and the individual properties of the fibers and the matrix [16].

2.2 GLASS FIBER REINFORCED POLYMER (GFRP):

The fibrous polymeric composites depending on the type and nature of the fiber constituents constitute an important branch of modern engineering materials. The glass fiber reinforced polymer (GFRP) finds its use in thermal and electrical insulation and structural support. The inclusion of glass fiber which is relatively less costly compared to carbon fiber also reduces the over all cost of the hybrid composite [17]

Glass fiber reinforced systems are responsible for the majority of the fiber reinforced plastic (FRP)/ polymer matrix composite (PMC) market in spite of the advent of higher performance and higher cost of carbon and aramid fibers. However the ongoing research follows the development and use of carbon fibers particularly for defense applications.

Although having lower specific values (i.e. modulus/density and strength/density ratios) than carbon fiber reinforced polymer (CFRPs), GRPs have adequate combinations of properties at an acceptable manufactured cost to suit many applications and in some cases are the preferred material compared to CFRPs (e.g. toughness requirement in small boats, insulation requirement in electrical applications. The properties of GRPs also show lower levels of anisotropy for the same fiber format than carbon fiber reinforced systems; which may make design easier.

2.2.1 MAJOR CHARACTERISTICS OF GFRPS:

The major characteristics of GFRPs are

(i) Good Corrosion Resistance

(ii) Light Weight

(iii)Good Toughness

(iv) Good Insulation property

(v) High Specific Strength

(vi) Process Freedom

(vii) Shape Freedom

In many cases, GRPs are used for a combination of these properties which with the flexibility and ease of processing can lead to unique design solutions [10].

2.2.2 APPLICATIONS OF GFRP

Fiber reinforced composite materials are being more widely used in many applications. With the increasing applications of these materials more and more knowledge is needed to get a better understanding of the materials which can lead to different mechanical properties of the materials [18]. The fatigue crack propagation properties of glass/epoxy composites has been of great importance since such composites are often used for engineering components that are subject to cyclic loading that can cause subcritical crack propagation resulting in the catastrophic failure [19].

Applications vary significantly in size, complexity, loading temperature, surface quality, suitable production volume and added values. Common driving forces for the use of GFRP materials include the ability to save weight, increase mechanical properties, reduce the number of elements in a component, obtain a unique combination of properties, and to increase shaping freedom. GFRP composites are used in following industry.

Aerospace industry: The high specific stiffness and strength of the reinforcement offered the potential for reduced fuel consumption and increased performance for military aircraft. The ability to tailor thermal expansion together with the low material density also made materials attractive for space applications. The main driving forces for the aerospace industry are therefore primary weight reduction by using a material with higher specific mechanical properties.

Transport industry: The transportation industry represents a potentially large applications area for fiber reinforced composites and is driven by a complex set of

increasing driving forces. The needs of the automobile industry have dominated the development of engineering composites with increased shape complexity and a strong emphasis on decreasing system cost. In the automobile industry the current use of composites is dominated by relating low fiber volume fractions and randomly oriented fiber architectures, for exterior panels, under bonnet parts and semi structural sub surface parts.

Other Industry: Branches such as the Leisure, building and marine industries are also significant users of composites in a diverse range of materials, processes and applications with wide range of driving forces. The Leisure industry includes the uses such as ball game rockets and clubs, bicycle frames, fishing rods and water sports boards. Both specialized low-volume and highly automated mass production technologies are used with a variety of materials [20]

Today over 95% of commercial reinforcement glass fibers are made from E-type [22].In the recent years the glass fiber reinforced polymers (GRP) specially glass/epoxy composites are widely applied in several civil engineering applications ranging from seismic retrofit of columns and strengthening of walls, slabs to new building frames and bridges[23]. Composite materials have been widely used in the ship building industry for four decades now mainly due to the distinct advantages they offer over more conventional materials such as aluminium and steel. The most important drawback is their susceptibility to out-of-plane impact damage such as that imparted by the accidental fall of a tool [6].

Composite pipes are being increasingly on demand by offshore oil and gas companies, where glass-fiber reinforced resin matrix composites are used to advantage in respect to the common steel pipes for the transport of service waters. In fact, the cost of installation and maintenance of composite pipes is reportedly lower than that of steel pipes. One can also cite the lower density and hence weight savings on the final structure and corrosion resistance of resin composites as the other advantages over steel pipes [24].

In the construction arena, and this is the focus of the present research, GFRPs have been employed due to their life-cycle cost competitiveness as reinforcing elements in Portland cement concrete environment with pure water, as structural shapes for non corrosive environments such as bridge decks, building columns, sewage treatment plates and in the repair of deteriorated concrete or wooden structures by wrapping with fiber-reinforced polymer (FRP) outer layers to enhance strength, stiffness and seismic resistance of structures. Thus FRP bars are used in place of steel to reinforce. Concrete bridge decks and indeed, the bridge deck itself can be made entirely of FRPs. Concrete columns and beams have been reinforced by wrapping with glass-reinforced epoxy. Wide spread utilization of FRPs in construction has however been hindered by the lack of long-term durability and performance data on which to base design calculations, especially when it is realized that FRP composites used in infrastructure applications are intended to have a service life in excess of 50 years. The FRPs used in construction are typically GFRPs due to the relatively low cost of glass fibers [25].

2.3 GLASS FIBER:

Today glass fiber reinforced plastic (GFRP) composites are high volume commodity materials. New markets for GFRPs in both transportation and infrastructure applications promise to accelerate the demand for glass fibers well into the twenty first century. According to the presence of different oxide composition glass fibers are of many types.

The main compositions of E-glass (electrically conductors) are the oxides of silica, aluminium and calcium. The glass fiber is also regarded as calcium alumino borosilicate glass. A-glass is a sodalime silicate glass that is less expensive than E-glass, but has much poorer electrical properties. D-Glass is a borosilicate composition developed for low dielectric constant in certain high performance electrical application. ECR-glass is a calcium alumino silicate with maximum alkali content of 2% and with properties similar to E-glass, except it is more corrosion resistant in acidic environment. AR-glass is an alkali zirconium silicate composition, which provides a greater alkali resistance necessary in cement and concrete reinforcement. S-glass is a magnesium alumino silicate glass except it is more corrosion resistant in acidic environment. AR-glass is an alkali zirconium silicate composition, which provides a greater alkali resistance

necessary in cement and concrete reinforcement. S-glass is a magnesium alumino silicate glass that delivers the highest combination of mechanical, thermal and chemical properties of all commercially available glass fibers. It is used primarily in aerospace and military applications.

The composition ranges for a given type of glass are broad enough that different properties are obtained from batches made from one end of the composition range to the other. Today over 95% of commercial reinforcement glass fibers are made from E-type compositions.

2.3.1 BULK FIBER STRUCTURES

Glassy materials have no crystallinity or long range order, i.e. they are amorphous. All glass fibers used in GFRP are silicates. In these glasses silica forms a three dimensional network of Si-O bond from the fundamental building block of $[SiO_4]^{4-}$ tetrahedral. The oxides in glass fiber are classified into three groups according to their function in the network structure. Other than silica, boric oxide is only other network former, with a polyhedral structure that connects with silica network. Aluminium, Titanium, and Zirconium oxides provide cations that can substitute for silicon in a network tetrahedron, contributing to the network stability; they are called "intermediates". All the remaining oxides in the table are termed "modifiers" because they can form only one or two chemical bonds and thus they can disrupt the network structures. Each monovalent sodium ion forms an ionic bond with a nearby oxygen atom, thus disrupting the covalent network.

2.3.2 BULK FIBER PROPERTIES:

The softening point is the temperature at which the glass will readily flow under its own weight and the strain point is identical to the glass transition temperature. The values are related to the extent of three dimensional network structure that results from the specific glass composition. Monovalent cations (sodium and potassium) lower the glass transition temperatures by disrupting the network. On the other hand, more tetravalent silicon leads to higher glass transition temperature glasses (quartz glass represents the upper limit). Higher temperature glasses require more energy to process,

and are generally more difficult to manufacture, resulting in higher costs. This is why S-Glass fibers are five times more expensive than E-Glass fibers. The electrical properties are typical for inorganic, non conducting materials. E and D-Glass were developed especially for cost effective and high performance electrical insulation and dielectric properties respectively. E-Glass is over three orders of magnitude more electrically resistive than A-Glass. D-Glass has by far lowest dielectric constants and dissipation factors. The thermal properties of glass fibers differ significantly from those of bulk glass, due to relaxation of the metastable, super cooled liquid state frozen into fibers during formation. The thermal expansion values apply to fibers only during cooling and during heating up to about 100^0C. Relaxation shrinkage in fiber length begins at about 100^0C and becomes dominant above 400^0C. Fibers show stag exothermal from about 100^0C to 500^0C and no glass transition; whereas bulk glasses have sharp endothermic glass transition peaks around 600^0C and no exotherms. Chemical durability of glass fibers plays an important role in GFRP. The weight loss of glass in water is proportional to the amount of higher soluble cations. The leaching mechanisms are very different in acidic verses basic media. In acid, removal of cations other than silicon begins rapidly, but slows down as a barrier of leached glass is formed. AR and ECR glass composites are more resistant to acid leading and fiber strength reduction under static loading conditions. The reduction in fiber strength seems to be associated with cracking in a brittle surface layer, which has been depleted in cations and is relatively porous as a result. Basic solutions on the other hand, effectively attack the silica network, but some of the metal oxides can be reprecipitated on the fibers in static solution tests, leading to ambiguity in interpretation of the weight loss data. That problem can be avoided by determining the tensile strength after exposure to either acidic or basic solutions, although the experimental work involved is difficult and time consuming. The high silica S-Glass fibers show no decrease in strength from PH. 1 to 11; where as E-glass fibers degrade in strength significantly either above or below a PH of 6. When considering the durability of GFRP composites, different questions to bear in mind. First, matrix resin may be influenced differently by the exposure. Second, the sizing layer that coats commercial glass fibers has a significant influence on the kinetics and mechanism of weight loss in solution. Third, in a GFRP composite, the solution has to diffuse through

the matrix to reach the fibers, which is likely to change the solution composition significantly. Finally, the way fibers are loaded and fractured inside moisture saturated.

In E-Glass, thermal compaction of the fiber structure leads to an increase in modulus at 538^0C. Poisson's ratio for E-glass fiber is 0.22 and S-glass is 0.23. The Young's modulus of thermally compacted glass fibers decreases slowly with increasing temperature [26].

2.3.3 SIZING OF GLASS-FIBER:

The hydrolytic stability of glass-reinforced composites is markedly improved by treatment of the glass with a dilute solution of an organo-functional silane. This operation is regarded as sizing. Considering the extreme hydrophilicity of clean glass surface, it can be inferred that chemical bonding has occurred between the glass and the silane, resulting in some type of protective layer. The selection of the proper silane and treatment conditions can enhance the mechanical properties of the composite in the dry state, as well, which implies a degree of interaction between the silane and the matrix resin. Commercial silanes have the general formula, X_3Si-R, where X is a hydrolysable group such as chloro-, methoxy-, or ethoxy-, and R is an organic group such as vinyl, -aminopropyl, or –methacryloxypropyl, which is compatible with the matrix resin. The X-groups are hydrolyzed in aqueous size solutions to give tri hydroxyl silanols. These silanols are attached to the glass surface by hydrogen bonds. When the sized fibers are dried, water is removed, leaving a polysiloxane layer against the glass surface and an outer polymeric layer rich in R-groups. During the curing process the R-groups react directly with functional grups in the matrix resin, forming covalent bonds. Chemical bonding between the siloxane and the glass should result and brittle to withstand the thermal stresses associated with processing. The water present during processing hydrolyzes the covalent silicon-oxygen bonds on the glass surface permitting the fiber and the matrix to slide past each other without permanent bond rapture. After the processing strains have been repeated, the chemical bonds can reform, restoring the integrity of the interface [27]. It is generally recognized that bond strength variation at fiber-matrix interfaces greatly affects the mechanical properties of composite materials. On the other hand, bond strength depends strongly on the chemical/molecular features,

atomic composition and topographical nature of fiber surface layers, which is strongly influenced by modification of fiber surfaces (sizing), since the silane coupling agent improves the bond quality [28].

2.4 EPOXY RESIN

Epoxy resin is relatively low molecular weight pre polymers capable of being processed under a variety of conditions. Two important advantages of these resins over unsaturated polyster resins are: first, they can be partially cured and stored in that state, and second they exhibit low shrinkage during cure. However, the viscosity of conventional epoxy resins is higher and they are more expansive compared to polyester resins. The cured resins have high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to variety substrates, and good electrical properties. Their major limitation is high cure time and poor performance in hot-weight environments. Approximately 45% of the total amount of epoxy resin produced is used in protective coatings while the remaining is used in structural applications such as laminates and composites, tooling, molding, casting, construction, adhesives, etc. Epoxy resins are characterized by the presence of a three-memebered ring containing two carbons and an oxygen (epoxy group or epoxide or oxirane ring). A range of epoxy resins is now available, varying from relatively tough low temperature epoxies for use in construction industry to brittle epoxies useful in aerospace sector. This widespread application of epoxy resins is primarily due to the availability of resins with different backbone structures and molecular weights to gibe products with low viscosity (liquids) to low melting point solids. The ease of process ability, good melting characteristics, excellent adhesion to various types of substrates, low shrinkage during cure, superior mechanical properties of cured resin, and good thermal and chemical resistance have made epoxy resin a material choice in advanced fiber reinforced composites. The polymeric network structure of epoxy resin is shown in fig: 2.1.

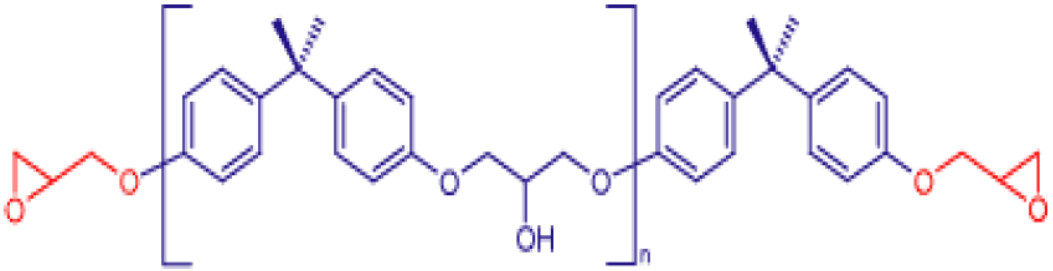

Fig: 2.1 (Network structure of epoxy resin)

2.4.1 CURING AGENTS

Optimum performance properties can be obtained by cross-linking the epoxy resins into a three dimensional and infusible network. The choice of curing agent depends on processing method, curing conditions, i.e. curing temperature and time, physical and chemical properties desired, toxicological and environmental limitations, and cost. The epoxy group, because of three membered ring structures, is highly reactive and can be opened up by a variety of nucleophilic and electrophilic reagents. Curing agents are either co-reactive or catalytic. A catalytic curing agent functions as an initiator for epoxy resin homo-polymerization, whereas the co – reactive curing agent acts as co-monomer in the polymerization process. A variety of curing agents containing active hydrogen atom such as aliphatic and aromatic amines, polyamide amines, polyamides, anhydrides, dicyandiamide, isocyanate, polysulphides, mercaptans, melamine – formaldehyde, urea formaldehyde, etc. have been used.

2.4.2 CURING OF EPOXY RESIN

The curing of epoxy resins is associated with a change in state from a low molecular weight liquid mixture to a highly cross-linked network. The molecular mobility in the system decreases as the curing proceeds due to cross-linking of several chains into network of infinite molecular weight. The sudden and irreversible transformation from a viscous liquid to an elastic gel is known as gel point. Gelation typically occurs between 55-80% conversions. Beyond the gel point, reaction proceeds towards the formation one infinite network with substantial increase in

crosslink density, T_g and ultimate physical properties. Vitrification of the growing chains or network occurs when the glass transition of the network becomes coincidental with the cure temperature. Vitrification is a reversible transition and may occur at any stage during cure. The cure may be resumed by heating to devictrify the partially cured epoxy resin. The reaction of amine and oxyrane ring is highly exothermic. The B-stage resin is partially cured resin where cross-links exist at widely spaced points. The hardness and thickness of such resin depend on the degree of cure advancement. By lowering the temperature, the curing reaction can be slowed down. The B-staged resin and prepages can be stored at low temparatures and can later be transformed ino a hard insoluble cured resin/laminate by completing the cure at elevated temperature. Amine cured epoxy networks generally form from epoxide-amine nucleophilic addition reaction at low cure temperatures. During the curing of epoxy resins by multi functional amines, the amino group and a secondary amino group open the oxirane ring and a hydroxyl group is produced. The primary and secondary amino groups are of unequal reactivity.

2.4.3 PROPERTIES OF CURED EPOXY RESIN

2.4.3.1 Glass transition temperature:

The macroscopic glass transition phenomena occur over a relatively wide temperature region. The T_g of cross linked polymer may be related to the overall conversion, stiffness of the cross linked chain, and the free volume entrapped in the network. The T_g depends predominately on the rigidity of the molecule. For rigid and constrained molecules, higher temperatures are needed to allow for the molecular motions associated with the deformation of material. The thermal expansion coefficient in the glassy state is the highest for the most highly cross linked sample while in the rubbery state it is the lowest.

2.4.3.2 Mechanical properties:

It was thought that the initial cure of the resin may affect the extent of degradation in the mechanical properties during exposure. The mechanical properties of cast epoxy resins depend upon the chemical structure of curing agent and epoxy

resin, epoxy-amino stoichiometry, cross linking density, curing schedule, test temperature and strain rate. The major problem with epoxy resin is its low strain-to-failure, high moisture uptake due to presence of polar groups, and poor retention of properties in hot wet environments. T_g and modulus of the cured resin is decreased in presence of moisture. An improvement in the yield stress and toughness is observed with increase in cure time from conventional 2 hr to 14 hr. this has been attributed to the greater extent of cross linking and the development of resin molecular structure through molecular rearrangement.

2.4.3.3 Tensile Stress-Strain Behavior

(i) *small-strain properties*: In the glassy state, at room temperature the small strain properties, like stiffness and yield point, show some influence of molecular architecture but predominately are related to intermolecular distance. Cross-link density does not appear to be important for these properties. The effects of stoichiometry on these parameters are rather small. As temperatures increases, the samples with low T_g show a relatively larger decrease in parameters. In the rubber like state, the stiffness predominately is governed by cross-link density and shows a much wider variation within each set of samples.

(ii*) Large strain Properties*: in the glassy state, the large strain properties like strength and elongation-to-break are affected intermolecular packing, molecular architecture, and molecular weight between cross-links. The overall molecular weight is also important. The regularity and perfection of the network also plays an important role. As temperature increases, the samples with low T_g show a relatively large change in these parameters. In the rubber like state, cross-link density appears to be important factor.

2.4.3.4 Moisture Transport

One of the major limitations of epoxy resins is their poor performance in wet environment. Water molecules interact with specific groups within these resins. Water absorption initially plasticizes the matrix. This is followed by a reduction in tensile modulus and the detachment of the resin from the fiber in the composite. The

moisture sorption is related to the fractional free volume available in the epoxy resin. At higher temperatures the free volume is generated predominately through segmental motion occurring above T_g.

2.4.3.5 Physical Ageing

When an amorphous glassy material like cross-linked epoxy resin is cooling, as it approaches to T_g, has a significant effect on its molecular architecture. Above T_g, the actual volume of the sample adjusts itself and acquires a particular inter segmental separation and a specific number and size distribution of holes that are present at T_g become immobilized [10].

2.4.4 APPLICATIONS OF EPOXY RESIN

Epoxy resins find a variety of applications as adhesives, laminates, sealants, coatings, etc. the optimum curing temperature and the thermal stability of epoxy resin depend on the type of curing agent. The anhydride cured epoxy resins have excellent electrical, chemical, and mechanical properties and are used for electrical and electronic applications. Epoxies are used as binders in materials for construction. Filling of cracks in concrete structures is achieved by epoxies. In construction industry, for bonding and coating purpose, low temperature curing of epoxies is achieved by using thiols that exhibit higher curing rates. Epoxy based prepages have been used in numerous aircraft components such as rudders, stabilizers, elevators, wing tips, landing gear doors, radomes, ailerons, etc. [10]

The densely cross linked structures are the basic of superior mechanical properties such as high modulus, high fracture strength and solvent resistance.

However, this can irreversibly damaged by high stresses due to the formation and propagation of cracks. This leads to dangerous loss in the load carrying capacity of polymeric structural engineering materials [30]. Brittle thermoset resins, such as unmodified epoxy and polyster, may undergo only a limited extent of deformation prior to failure [31].

2.5 ENVIRONMENTS TO WHICH THE GFRP COMPOSITES ARE EXPOSED TO:

Laminated fiber-reinforced composite materials are widely used in the marine industry due to their good environmental resistance, the ease with which they may be formed into complex shapes, and also their high specific strength and stiffness. Composites are the dominant material for pleasure boat construction and are extensively used in the construction of fishing and naval vessels. High speed craft such as fast ferries and patrol craft are now an increasingly important part of the marine industry, and the use of light weight, corrosion resistant readily fabricated and formed composites is ideal for such fabrication. [32]

FRP structures, these can work in more or less aggressive environments i.e. temperature, humidity, corrosive environments, chemical exposition. Their sensitivity to the different environments parameters must be taken into account before putting them into service. In particular, when the humidity and the temperature act at the same time, they represent a danger to the long term stability of these structures. Temperature variation and humidity absorption cause an irreversible hygrothermal deterioration of the material [2].

A major advantage of GFRPs is that composite properties can be tailored by a judicious choice of design factors, such as fiber volume content, fiber architecture, type of resin, and the chemical nature of the sizing applied to the surface of the fiber. However, when optimized for a specific application, these additional tailoring advantages can become additional sources of concern when the composite materials are exposed to the environment. At the very last, one can anticipate that GFRPs will come into contact with atmospheric humidity, acid rain, deicing chemicals, and the alkaline environment in the proximity of Portland cement concrete. Any material is subject to microstructural and morphological transformations during its service life, leading to property changes due to physical and chemical ageing. It is possible that the presence of moisture in the composite, whether by itself or in combination with other chemicals, can initiate undesirable structural changes within the fiber reinforcement and the matrix or the interface, and this can potentially reduce the

durability of the GFRP [25]. The effects of environmental exposure of fiber-reinforced polymer composites (FRPC) and long term retention of properties are significant concerns for such applications, where the service life can span several decades and little or no maintenance is expected. To design for such for such service life requires the ability to forecast changes in material properties as a function of environmental exposure, including bulk properties and the integrity of fiber-matrix interfaces. [33]

Impact of environmental factors such as temperature and humidity on composite materials behavior is of significant concern for the aircraft industry since storage and operating conditions vary considerably and can add to the wear and tear of structural components [34]

The applications where corrosive environments are experienced by the material, further degradation of the mechanical properties can occur. The loss of strength or stiffness over time can produce unexpected material failure resulting in, at the very least, costly downtime or hazardous spills. [35]

A critical aspect of using fiber reinforced polymer matrix composites in various applications is their performance in 'hot-wet' environments. Composites with common structural polymer matrices often absorb moisture and this has preferred effects in their mechanical, thermal, dielectric and barrier property performance. It is therefore not surprising that experimental and theoretical work on moisture absorption in composite was and still is an active research topic across many disciplines. [36]

2.6 ENVIRONMENTAL DEGRADATIONS OF GFRPs:

Environmental exposure most often leads to matrix degradation, fiber/matrix de-bonding and delamination in polymer composites [23]. The use of composite in safety critical applications leads to uneasiness since the mechanical response is not well understood in active and complex environmental conditions. The nature and order of degradation by complex and active environments need to be critically

investigated to expand the acceptability of such type of PMCs like E-Glass/Epoxy composite. [37]

Damaging mechanics as applied to composites studies the onset and growth of damage tolerance criteria and establish monitoring protocols for the life time of composite structures. The principal types of damage that occur to composites are interlaminar cracking, interlaminar delamination, fiber breakage, fiber- matrix interface failure, and fiber pull-out. Environmental agents that cause damage to composites are electromagnetic effects, fire and high temperature, lightning and electrical discharges, chemical degradation, ultraviolet radiation, out-gassing at high vacuum, erosion by rain and sand, moisture uptake and contact with organic liquids such as fuels, lubricants and deicing fluids. During normal service aircraft are exposed to all these agents in a time variable manner. [38]

The mechanical properties of Glass fiber/epoxy composites under offshore oil pipes usage are greatly affected by UV exposure and water exposure. There are many degradative effects like plasticization of the polymeric matrix, reduction in T_g, swelling affects the fiber matrix interfacial strength. The long term behavior of composites during their service lives in aggressive environments must therefore be analyzed to guarantee a safe operational use of these materials. [24]

PMCs come across with the several of thermal environments; when they are exposed to use in day to day life. Again thermal expansion coefficients of polymers are substantially greater compared to metals and ceramics. This is why failure of the bond between fiber and resin occurs under the influence of temperature gradient. Thermal stresses caused by temperature gradient should be given special attention in many application areas. [39]

The focus of this project has been concentrated to understand the effect E-Glass/Epoxy composite under various environmental exposure like moisture and thermal exposure.

2.7 MOISTURE SORPTION PROCESS:

The sorption of solvents in polymeric composites and their effects on composites performance are highly complex issues. Polymers are highly complex materials that vary in structure and physico-chemical properties and polymeric composites adjoin an assortment of fibers with extremely intricate fiber/matrix interphases and interfacial bonding which is already a complex situation. The complexity is further compounded by the ingress of fluids of many kinds, which interact differently with the polymer, the fiber and the interface within the composite. [40]

PMCs absorb moisture when these composites are susceptible to heat and moisture when operating in changing environmental conditions. The environmental action such as high moisture and high temperature can limit the usefulness of polymer composites by deteriorating mechanical properties during service. Impact of environmental factors such as temperature and humidity on composite materials behavior is of significant concern for aircraft industry since storage and operating conditions vary considerably and can add to the wear and tear of structural components. [30]

The kinetics of fluid sorption in polymers was studied by Fick in1855.

2.7.1 FICK'S DIFFUSION

The simplest model for the diffusion of solvent into solid is given by the linear Fick's diffusion.

Accordingly; the flux of the solvent F, is proportional to the concentration gradient ∇m .

In one dimensional cases

$$F = -D\frac{\partial m}{\partial x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

D = diffusion co – efficient

The negative sign in equation (1) indicates that the flux is directed from higher to lower concentration region.

According to conservation of mass principle

$$\frac{\partial m}{\partial t} = -\frac{\partial F}{\partial x} \quad \text{..... (2)}$$

Hence the combined concept of equation (1) and (2) must be in the form

$$\frac{\partial m}{\partial t} = D\frac{\partial^2 m}{\partial x^2} \quad \text{..... (3)}$$

Above equation is said to be the Fick's 2nd law of diffusion.

The diffusion process which obeys equation (3) is called Fickian type of diffusion.

The total weight gain $M(t)$

$$M(t) = \int_{-L}^{+L} m(x,t)dx \quad \text{..... (4)}$$

Where $m(x,t)$ = concentration of moisture which depends upon the position of the sample and time of diffusion. [40]

2.7.2 THE TEMPERATURE DEPENDENCE OF THE DIFFUSION CO-EFFICIENT

The temperature dependence of the diffusion co-efficient of diffusion can be expressed by an Arrhenius-type of relationship

i.e. $D = D_0 e^{-E_a/RT}$ ..... (5)

Where D = time dependence diffusion co-efficient

D_0 = pre exponential term or permeability index

E_a = activation energy of the diffusion process

R = gas constant

Slope of the curve for D Vs 1/a gives the value of E_a and the intercepts gives for the value of D_0 [41]. The assumption that the mass diffusion coefficient (diffusivity) depends only on temperature is expedient because in most practical situations it provides adequate, even though approximate, results. Nevertheless, it must be remembered that D may depend also on the concentration and the stress level inside the material. These factors may need to be taken into consideration in some applications [42].

2.7.3 WEIGHT GAIN (MOISTURE UP-TAKE)

The moisture absorption $M(t)$ can be determined from the weight gain of the specimen; as a function of time

$$M_t = \frac{w_t - w_0}{w_0} \times 100 \text{ ..... (6)}$$

Where w_0 and w_t are the weights of the dry and wet specimens at a time t respectively. [22]

An increase in temperature significantly accelerates the moisture diffusion. In reality, all resins and composites currently in use display two similar stages of diffusion model. These two stages of moisture absorption are assumed to be respectively diffusion and relaxation controlled. [43]

As the moisture content increases the rate of absorption decreases and approaches a maximum for a particular environment. There is usually a maximum temperature/humidity above which the moisture kinetics becomes Non-Fickian. [9]

As the natural process of moisture absorption in epoxy matrices is normally very slow. So Fick's 2nd law for a concentration independent moisture diffusion process for a long period of exposure in the solution can be approximated as

$$M = \left\{1 - \frac{8}{\pi^2} e^{-\pi^2 Dt / h^2}\right\} M_m \quad \text{..... (7)}$$

Where D = composite diffusion co-efficient

t = Time at maximum moisture content

h = specimen thickness

M_m = Maximum moisture content

Assuming that the moisture absorption process follows Fick's law; the apparent D can be determined as

$$D = \pi\left(\frac{h}{4} M_m\right)^2 \left\{\frac{(M_2 - M_1)}{\sqrt{t_2} - \sqrt{t_1}}\right\}^2 \left(1 + \frac{h}{L_e} + \frac{h}{d}\right)^{-2} \quad \text{..... (8)}$$

Where L_e and d are the length and width of the specimen respectively.

And M_1, M_2 are moisture contents at time t_1 and t_2 respectively. [23]

2.7.4 THE DIFFERENT STAGES OF MOISTURE DIFFUSION PROCESS:

In many circumstances weight-gain data for the sorption and desorption of fluids in polymers do not occur with the predictions of linear Fickian diffusion shown in figure: 2.2

Moisture weight gain data in polymeric composites exhibit departures/deviations from linear Fickian behavior along curves "A", "B", "C" and "D" in fig: 2.2 correspond to severe circumstances and are usually associated with irreversible damage and degradations. The solid line, designated by LF, corresponds to linear Fickian diffusion.

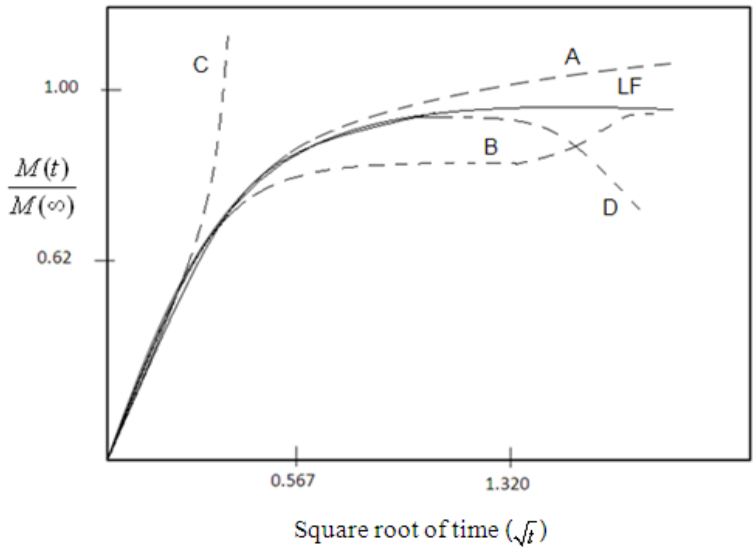

Fig: 2.2 (Schematic curves representing four categories of Non-Fickian weight gain sorption)

(i) Curve-A: - Denoted as "Pseudo – Fickian" – continuous gradual increase in weight gain – never attaining equilibrium.

(ii) Curve-B:- Two stage diffusion

(iii) Curve-C: - Represents to rapidly increasing moisture content within the composite which is usually accompanied by large deformations, damage growth, material break down and/or mechanical failures.

(iv) Curve-D: - Associated with weight loss data that is attributed to irreversible chemical or physical break-down of a material.

Most commonly, weight loses occur in conjunction with hydrolysis namely the separation of side groups from the polymeric chains and possible chain break downs, or the dissociation of matter located at the vicinity of fiber-matrix interfaces.

Due to the wide variety of polymeric molecular structures and the polymeric composite material systems it is impossible to make specific predictions that correlate the disparate sorption process typified by the different weight gain plots in fig: 2.2; with a particular causes. However; a comprehensive review of many data suggests the curve

“C” and “D” in fig: 2.2 corresponds most frequently to sorption processes that occur under severe circumstances, such as elevated temperatures, high external stresses, or under exposure to high levels of ambient solvent concentrations. The weight gain corresponds to curve-C associated with substantial degradations in material integrity is associated with Curve-D in fig: 2.2. [40]

2.7.5 FACTORS INFLUENCING THE MOISTURE DIFFUSION

THE NON-FICKIAN BEHAVIOR AND ITS CAUSE:

There is a host of possible reasons for non-Fickian diffusion on polymers and get additional probable causes when considering polymeric composites. The glassy polymers with their highly complex molecular configurations exist in non-equilibrium thermodynamic state accounts for their inherent time dependent behavior. The time dependence is accelerated by the fact the liquids tend to increase the free volume of polymers, thereby lowering the glass transition temperature. The increased mobility of the molecular chains and side group is the key factor for the Non-Fickian type of diffusion. The time dependent diffusion process occurs conjointly with the time dependent mechanical response of polymers, namely creep and relaxation. Accordingly the polymer requires time to approach to its new equilibrium state commensurate with extremely imposed boundary conditions.

Fluid saturation levels in polymers and polymeric composites may depend on the amplitudes of extremely applied loads. These saturation levels may increase with the magnitude of external tension. The hydrostatic compression may increase or reduce the uptake levels of fluids since external compression tends to drive more fluids into the composite, while decreasing the free volume entrapped within the polymers. In this case Fickian diffusion may deviate to the Non-Fickian type.

Another approach to account for Non-Fickian behavior is offered by the “two phase diffusion” model. A portion of the diffusing substance is entrapped within the polymeric molecules and whiles other part become immobile. Here the complete desorption can’t predictable on drying. That means some moisture again diffuse. The concentration

dependent diffusivity is the cause of Non-Fickian diffusion. Here the Fick's diffusion equation becomes non-linear.

A more intricate sorption process occurs when diffusion is accompanied by a chemical reaction. The chemical reaction can introduce an inert substance into host material. The solvent absorption is accompanied by an enhanced weight gain. On the other hand, the chemical reaction may involve dissociation of matter thereby diffusion induces weight loses. The deviation of Fickian type to Non-Fickian may occur after substantially long exposure times. Such type of deviations occurs due to extremely slow chemical reactions.

Chemical reaction may destroy the polymer chains and dissociate them into separate segments. The phenomenon "hydrolysis" is irreversible and would usually result in the leaching of matter, thus resulting in a weight loss. Alternatively hydrolysis may have the contrary effect of inducing micro cracks within the composite and lead to excess weight gains. The induced micro cracks set as the further diffusing sites for the moisture diffusion process. Again the severity of the hydrolysis process increases with temperature and solvent content and depends on the material system. The onset of hydrolysis may require some "incubation time" whose duration depends on temperature and solvent concentration as well.

Temperature affects moisture absorption in several aspects. As diffusion is thermally activated process an increase in temperature accelerate the short term diffusion and the diffusion coefficient.

Osmosis may the cause of diffusion in glass fiber/epoxy composite where polymer serving as a semipermiable membrane. The effect of osmotic pressure may be compound by the micro level tensile stresses caused by the mismatch in mechanical and expansional properties of the resin and fiber materials.

The formation of interfacial cracks as well as voids may be the primary cause for an increase in the amount of solvent absorbed by the composites resulting in a transitional from Fickian to Non-Fickian. However, the forgoing increase is most likely due to the incursion of solvent into the micro cracks and micro voids, rather than to an enhanced

diffusion from newly formed internal boundaries. The cyclic exposure to wet/dry environments increased the extent and amount of interfacial fiber/matrix cracks which is the cause of further moisture diffusion. This leads to the Non-Fickian type of moisture diffusion [40]. A concentration driven osmotic process is responsible for moisture absorption into the matrix of the composite under hydrothermal ageing condition [44]. Assbee et.al. [45] have actually illustrated etching on the surface of glass fibers. They have differentiated three glass fiber types on the basis of correlations between alkali content and fiber de-bonding considered resulting from osmotic pressure. They proposed osmosis of the interface by alkali metal oxides leaching from E-glass in the presence of moisture.

The diffusion of penetrant molecules into polymers depends on two factors, namely

(i) The availability of appropriate molecular size holes in the polymer network
(ii) The attraction forces between the penetrant molecules and the polymer.

The presence of holes is determined by the polymer structure and morphology reflected in its degree of crystallinity, cross linking density, molecular chain stiffness and ability to closely pack in amorphous state. The formation of an appropriate hole also depends on the polymer and on the size of the penetrating molecules. Water molecules are hydrogen bonded and form clusters within the polymer. Thus the first factor affecting diffusion process is essentially a geometrical one. The second factor concerns the chemical nature of the penetrant verses that of the polymer. This factor determines the penetrant-polymer affinity. The relatively high water absorption capacity of epoxy resins derives from the presence in the epoxy chains of –OH groups attracting the polar water molecules.

The coefficient of moisture diffusion into epoxy resins depends on four main factors as follows:

(i) The polymer network structure
(ii) The polymer polarity determining polymer-moisture affinity
(iii) The physical morphology of the polymer
(iv) The development of micro damage under severe humidity condition

According to Morom et.al; it is difficult to predict which of these factors or a combination these of dominates the moisture diffusion process into a given epoxy resin [41].

Moisture absorption is matrix dominating property in fibrous composites. The structure near the interface is different from bulk matrix; so this leads to composite absorbing different amount of water per unit mass than the bulk polymer. The amount of water absorbed at the interface also depends upon nature of the glass surface, i.e. lower the functionality of the silane is higher the cross-linking density at the interface and lesser will be the amount of moisture absorbed. Moisture penetration at the interface contributes free volume of mesoscopic origin in addition with the one existing in the bulk of the matrix phase. There are two main mechanisms of moisture penetration involved, first one is moisture diffusion into the matrix and second mechanism is moisture diffusion along the fiber matrix interface by capillary flow. [37]

Higher temperature accelerates diffusion rates of moisture and generally accelerates ageing. [33]. Epoxy resin absorbs water from the atmosphere with the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of the water into all the material. The water absorbed is not usually in the liquid form but consists of molecules or groups of molecules or groups of molecules linked by hydrogen bonds to the polymer. In addition; liquid water can be absorbed by capillary action along any crack which may be present or along the fiber-matrix interface. The absorption and desorption curves when plotted are always concave towards the time axis and asymptotically reach the equilibrium value. But, the diffusion behavior of glass does not obey the Fick's law. Deviation from Fickian's law becomes more pronounced at elevated temperature and for material immersed in liquids. [43]

2.7.6 MOISTURE TRANSPORT IN POLYMERS:

The mechanism of moisture diffusion in epoxy has been studied by Luo et.al. Moisture transport in polymers is related to molecular sized holes (nano voids) within the polymer matrix and to the polymer matrix-water affinity. There are two states of water in the water-absorbed epoxy system. The unbound free water; filling the nano

voids, does not cause swelling. Hydrogen bonded water on the other hand, causes swelling of the polymer. The amount of volume changes due to the moisture induced swelling is significantly less than the volume of moisture absorbed, indicating that a large portion of absorbed water resides in the nano voids. Although amino and hydroxyl groups in epoxies have a strong affinity to water, not every of these polar groups attracts a water molecule. This is due to the formation of hydrogen bonds between these polar groups on polymer chains. The polarity of polymer affects the diffusion of water. However, it has not been established up to what extent the topology has a significant effect on the moisture diffusion. The mobility of water in a polymer matrix and absorbed water affects the mobility of polymer chains at temperatures below and above $T_{g.}$ the blocking of moisture transport can be explained by this cause. Water in the nano voids (molecular sized holes) may form hydrogen bonds with polymer chains and thus the nano voids blocked and water transport is reduced. [22, 46]

The primary mechanism of moisture pick up by the FRP composites is surface absorption and diffusion through the matrix is given by Fick's second law of diffusion. The water absorption behavior is affected by two competitive processes 1) Hydrolysis, which tends to subtract water to the diffusion process and 2) Hydrophilisation, which results in increased uptake of water through swelling and plasticization [47].

Transport phenomena in polymers are generally explained by a number of free volume-based theories. In case of impermeable fiber based composites (glass/epoxy); the diffusion co-efficient and the equilibrium moisture content decreases with fiber volume fraction. The fiber orientation to the diffusion has a significant effect.

In an impermeable fiber based polymer composite; the diffusion of the moisture takes distorted path as characterized by the following equation.

$$K= 1/ \beta\xi$$

Where K= structure factor which decides the dependence of the diffusion co-efficient on the structure of the given composite.

β = turtuosity factor

ξ= polymer chain immobilization factor.

Thus, in an impermeable fiber polymer composite; the fiber impedes the diffusion process [43].

2.7.7 EFFECT OF MOISTURE DIFFUSION ON E-GLASS/EPOXY COMPOSITE

In certain cases, moisture diffusion is helpful to the FRP composites. The siloxane network does not cover the glass fiber continuously as a monolayer film. It rather forms islands of three dimensional networks on glass fiber.

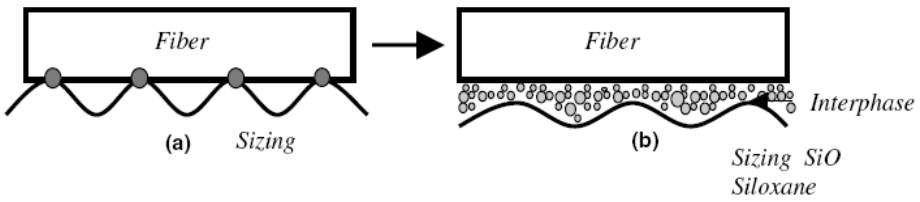

Fig: 2.3 (a) Control specimens, (b) Conditioned specimens with hydrogen bonds [48]

The presence of water in the matrix and at the interface in conjunction with the axial load increases, the effective contact area/region between fiber and matrix in which strong physical interactions can create adhesion between fiber and matrix. Although the chemical bonds between fiber and matrix break; the presence of water can create a region where larger surfaces of fiber and matrix participate in the adhesion process as shown in fig: 2.3. The larger contact area/region allows the load to transfer to the fiber more effectively thus maintaining the strength. But here the modulus of the material decreases. [48]

The absorption of moisture to E-Glass /Epoxy composites causes degradation of matrix dominating properties such as inter laminar shear strength, in-plane shear strength, compressive modulus and fracture strength. [37]

Chemical degradations include matrix hydrolysis and fiber degradation in some cases. Physical degradation involves plasticization and swelling of the matrix.

The environmental degradation that occurs in a FRP-composite is linked directly with the amount of moisture that is absorbed. The polymeric composites undergo dilatational expansion when absorb moisture in humid environments. The presence of moisture and the stresses associated with moisture-induced expansion may lower the damage tolerance and structural durability [30]. These effects are generally reversible when water is removed but high temperature exposure can produce irreversible effects which cause chemical degradation of the matrix and attack on the fiber-matrix interface which lead to de-bonding in the interface and micro cracks in the composite [5, 23]. Further there may be increase in internal voids, chain expansion and micro cracks formation into the matrix. In many cases, during initial sorption period the glass transition temperature increases. According to Sharma et.al this may be due to formation of strong double hydrogen bond in the epoxy matrix or at the interface [37]. It was also reported that water at the interface causes replacement of covalent bonds between the siloxane backbones of the sizing material on the glass surface with strong hydrogen bonds between the glass surface, water molecules and the network of silane coupling agents. [28]

The degradative effects are summarized below.

2.7.7.1 Plasticization

Moisture (water) that diffuses into the composite ends up either in the matrix or at the interphase region. In the matrix, water would act as a plasticizer, increasing free volume, lowering glass transition temperature and relieving the internal stress that was built up during processing of the composite. This phenomenon called plasticization in turn may lower the modulus since the matrix became pliable due to the presence of the plasticizer. Differential co-efficient of thermal expansion between fiber and polymer further develop residual stresses at the interface. These stresses along with the internal stresses relieved by plasticization weaken the brittle thermoset epoxy resin and/or the interfacial region of laminate. [30]

2.7.7.2 Swelling

With swelling, the liquid or solute diffuses into and is absorbed within the polymer; the small solute molecules fit into and occupy positions among the polymer molecules. Thus the macromolecules are forced apart such that the specimen expands or swells. Furthermore, this increase in chain separation results in a reduction of the secondary intermolecular bonding forces; as a consequence, the material becomes softer and more ductile. The liquid solute also lowers the glass transition temperature and, if depressed below the ambient temperature, will cause a once strong material to become rubbery and weak. Swelling may be considered to be a partial dissolution process in which there is only limited solubility of the polymer in the solvent. Swelling is affected by temperature as well as characteristics of the molecular structure. In general, increasing molecular weight, increasing degree of crosslinking and crystallinity and decreasing temperature result in a reduction of these deteriorative processes [11].

Differential strain which is created by the expansion force exerted by the liquid while stretching polymer chains at the cross linking density decreases at the result of which free volume entrapped within the polymer increases. So modulus decreases [30].

2.7.7.3 Hydrolysis

Water at the interphase causes replacement of the co-valent bonds between the siloxane back bone of the sizing material and the glass surface, with hydrogen bonds between the chemical moieties on the fiber glass surface (moieties containing oxygen atoms),water molecules at the interphase, and the hydroxyl groups on the sizing material. The absence of co-valent bonds at the interphase leads to clear de-bonding of fibers from the matrix. [48]

The adverse effects of moisture described above affects the fiber-matrix adhesion properties, resulting de-bonding at fiber/matrix interfaces, micro cracking in the matrix, fiber fragmentations, continuous cracks and reduction in ILSS (Inter Laminar Shear Strength) and several other phenomena that actually degrades the mechanical property of the composite.[23]

My main focus on this project is to concentrate on the reduction of ILSS, Micro structural damage and reduction in glass transition temperature due to moisture absorption.

2.7.8 REDUCTION IN ILSS DUE TO MOISTURE ABSORPTION:

It is the maximum shear stress existing between layers of laminated material.

The formula for Inter Laminar Shear Strength is given by

$$\text{ILSS} = 0.75 \; p_b / bt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where p_b = breaking load

b = width of the specimen

t = thickness of the specimen. [49, 50]

The ILSS of moisture exposed specimen increases for shorter durations of conditioning. Because the hygroscopic (swelling) stresses which are being developed during the conditioning counteract the curing stresses, resulting in a lower amount of resultant residual stresses which are opposite in nature. When the conditioning time increases, correspondingly the ILSS gradually decreases due to plasticization and swelling [23].

The shear failure mechanism is generally explained by a combination of resin swelling, plasticization and lowering of glass transition temperature of epoxy resin as it absorbs moisture. There is also embrittlement linked to the degradation of macromolecular skeleton by hydrolysis, osmotic cracking, hygrothermic shock for the change of water level and localized damage at the fiber/matrix interface. The more deleterious effect of freezing treatment is irreversible in nature [5].

The ILSS decreases with subsequent moisture absorption when measured at room temperature. It is earlier noted that the ILSS decreases by 25% when it has absorbed a maximum amount of moisture (~ 2%) [43].

2.7.8.1 PARAMETERS AFFECTING ILSS:

2.7.8.1.1 Effect of frozen moisture content on ILSS:

The shear strength value of frozen moisture conditioned specimen is less for the same time of exposure compared to that of only hygrothermally conditioned specimen for both type of loading speeds (i.e. lower and higher loading speeds). The moisture pick-up leads to the development of hygroscopic residual stresses along with other damaging effects. When the absorbed moisture gets frozen inside the composite specimen, this may lead to volumetric expansion of absorbed moisture and consequently further swelling stress development in the polymer composite.

2.7.8.1.2 Effect of Loading Speed:

The ILSS verses exposing time curves become convergent at a higher level of exposing time in both hydrothermal/hygrothermal conditioning. The nature of behavior may be attributed to the fact that at higher levels of absorbed moisture; the degradation of epoxy/interphase is higher. The more time available during lower loading speed may cause the absorbed moisture to move through the cracked channel, developed during testing, and thus causing further moisture/matrix interaction. This result in more deterioration and thus lower values of ILSS are observed. [5]

The differential change in the condition of constituent phases (fiber, matrix resin and interphase of fibrous polymer composite in such harsh and hostile environments can result in a significant mismatch among constituents and thus eventually leads to the evolution of localized stress and strain fields in composite.

2.7.9 REDUCTION IN GLASS TRANSITION TEMPERATURE (T_g):

The glass transition temperature (T_g) of a polymer is the temperature above which it is soft and below it is hard. Glass transition temperature (T_g) of thermoset matrix in composites is very important property because it defines the critical service temperature of the component and consequently their applications. For practical applications they are used at a temperature below their T_g i.e. in the glass state. For

epoxy resins, T_g is the temperature at which the polymer goes from glassy to a rubbery solid. Practically in case of resins it is a temperature region rather a single point. At T_g, a very rapid change in property takes place. So it is very difficult to estimate it precisely.

At and below the glass transition temperature $1/40^{th}$ of the total volume of the material is free volume. Taking this into consideration; T_g will be lowered when a polymer is mixed with a miscible liquid having more free volume, such that the diluent – polymer solution will contain more free volume at any given temperature. As a result; the polymer must be cooled to a lower temperature in order to reduce its volume to $1/40^{th}$ of the total volume of the process when moisture absorption takes place into the exposed resin.

So the T_g for plasticized system

$$T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d (1 - V_p) T_{gd}}{\alpha_p V_p + \alpha_d (1 - V_p)}$$

Where T_{gp} = Glass Transition temperature of the polymer

T_{gd} = Glass Transition temperature of the diluent

α_p = Expansion co-efficient of the polymer.

α_d = Glass Transition temperature of the diluent.

V_p = Volume fraction of the polymer

Again $V_p = \left[1 + \frac{\rho_p}{\rho_d} \{(0.01)M\} \right]^{-1}$

ρ_p = Density of the polymer

ρ_d = Density of diluent

M = percentage of weight gain [23]

When the temperature of the polymer is raised, it passes from a glassy state, in which it behaves essentially as an elastic solid, and is relatively stiff and non-dissipative, to a rubbery state, in which it behaves more like a highly viscous fluid, with a very low stiffness and also a low loss factor. The transition from a glassy to rubbery state is accompanied by a rapid fall in modulus, and a peak in the damping, or loss factor, of the material [51]. Water in an epoxy in its rubbery state above the glass transition has a much higher mobility than in a polymer in its glassy state. The presence of moisture has no significant effect on the polymer chain mobility at temperatures below the reduced glass transition temperature [46].

Considering the progression of cure and increase in T_g with time for the "ambient" specimens, it is important to keep in mind the competing effects of cure progression and environmental exposure. It may, therefore, be more instructive to consider a comparison of glass transition temperature after exposure to an environmental condition to that of the "ambient' over the same time period as

$$\%change = \frac{(T_g)_{after} - (T_g)_{ambient}}{(T_g)_{ambient}} \times 100 \text{ [52]}$$

2.7.10 Microstructural Damage:

P.K Ray et.al [23] investigated the surface morphology of moisture conditioned E–glass/epoxy composite. Here the moisture results in the loss of adhesion between the fiber and the matrix. B. Abdel-Magid et.al investigated that the failure in the moisture conditioned specimens occurred across the thickness of the specimen within gauge length, with massive de-bonding and fiber breakage. They investigated the surface morphology by taking Scanning Electron Micrograph between fiber and matrix at the interface or in the matrix. The micrographs taken by the workers show some degree of de-bonding at the fiber-matrix interface due to moisture absorption. Due increase of conditioning time, the failure occurred as multiple inter laminar cracks parallel to the fibers towards the middle of the cross-

section of the conditioned specimen [48]. The moisture is absorbed by the resin matrix causing it to swell to increase internal voids of the entangling polymer. This may result in microvoids or cracks in the matrix and resin/fiber interface [5].

2.7.11 VARIOUS MOISTURE ENVIRONMENTS:

The long term mechanical reliability and safety of composite material structures depends on the environment to which a structure is exposed [53]. There have been several efforts made by many researchers in the last few decades to establish a much needed correlation between mechanical property of the material and the moist environment or similar hydrothermal or hygrothermal environments that affects the moisture intake in a composite [23].

According to different applications of FRP composite in various fields, there exist different moist environments.

2.7.11.1 Hygrothermal Conditioning:

A common phenomenon; is the combined effect of moisture and temperature is so called hygrothermal effect [43]. Aerospace applications are included under this category of moisture absorption. The Hygroscopic nature of polymeric systems, however, necessitates a complete understanding of the interaction between structural integrity and hygrothermal environments [5, 34]. The resulting hygrothermal forces and residual stresses combined may be sufficiently large enough to influence the failure of laminated composite and thus should not be neglected in modern design and lifetime estimation. FRP composite structures are expected to experience a range of hygrothermal environmental conditions during service life. Since absorbed moisture can alter the stress state and degrade the interface, understanding of hygrothermal behavior is critical for predicting structural performance [30]. Hygrothermal ageing can promote thermo oxidative degradation in epoxy networks [49]. It is also widely acknowledged that hygrothermal ageing may significantly weaken the materials constituents (fiber, matrix and interfaces), thereby changing the mechanisms of first damage creation during fatigue loading [54]. When FRP composites are exposed to

hygrothermal environment for longer period, the T_g usually decreases and therefore, the service temperature of the material changes [55].

2.7.11.2 Hydrothermal Conditioning:

Several efforts made by many researchers to investigate about the mechanical property of the glass fiber/epoxy composite exposed to hydrothermal environments. P.K. Ray et.al maintained the temperature 90^0C for hydrothermal treatment to such type of composite. Applications under this effect are including marine components and structural bodies in civil infrastructure [23].

2.7.11.3 Sea Water Conditioning:

Exposure of composite structure in marine environments is to be simulated which studies the effect marine parameters on the structural integrity of the composite [23]. Applications under this effect including marine components such as masts, submarine control surfaces, transmission shafts and propellers [49, 56]. The oil industry is presently investigating the possibility of drilling for oil in the ocean at depths of 2000m and more. To recover oil economically from such depths, several new technologies must be developed. In addition to cost savings in terms of weight, composites have several other properties that make them attractive alternatives to steel in deep-water drilling applications. Composites have excellent fatigue properties, will not corrode in sea water, and have strengths similar to that of steel. Also, the fact that composites can be designed with certain properties in a specified direction can be exploited in the production riser where a low axial stiffness is desirable. A drawback to use composites in offshore applications is the lack of information concerning the long-term effects of sea water on composites. There have been a few studies in which specimens were aged under conditions similar to that of the ocean environment, and even fewer studies to investigate the long-term effects of such exposure. [57]

There is a small possibility of a steep rise in sea water temperature because of accidental fire due to lightning, electrical faults or high speed collisions. This can give rise to intense thermal stresses in the components around manufacturing and in-

service defects or cracks. The concentration of thermal stresses around these defects can result in catastrophic failure. The loss of adhesion and microstructural integrity at the fiber/matrix interface because of cyclic treatment may be reflected in the inter laminar shear strength (ILSS). [49]

Matrix and/or interface degradation resulting from moisture absorption is a concern in most composite applications subject to normal atmospheric moisture, which can range from precipitation to mild humidity. Complete immersion in water constitutes the most several environments, while humid air generally results in lower maximum moisture content. [33]

Thermal and moisture exposure lead to the matrix degradation, fiber-matrix de-bonding and fiber fracture. [53]. Hence my next attempt is to represent the literatures regarding the degradations occurred due to thermal shock applied to E-Glass /epoxy composites.

2.8 THERMAL SHOCK AND ITS EFFECT ON E-GLASS/EPOXY COMPOSITE:

Differential thermal expansion is a prime cause of thermal shock in composite materials. Thermal expansion differences between fiber and matrix can contribute to stresses at the interface. A very large thermal expansion mismatch may result in de-bonding at the fiber/matrix interface and/or a possible matrix cracking due to thermal stress. The performance of fiber-reinforced composite is often controlled by the adhesion chemistry at the fiber/matrix interface. Thermal expansion coefficients of polymers are substantially greater compared to metals and ceramics. That is why failure of the bond between fiber and resin occurs under the influence of temperature gradient. Thermal stresses generates in glass fiber reinforced epoxy composites by up-thermal shock cycles (negative to positive temperature exposure) for different durations and also by down-thermal shock cycles (positive to negative temperature exposure). The concentration of thermal stresses often results in weaker fiber/matrix interface. A degradative effect arises in both modes for short shock cycles and thereafter; also here is improvement in shear strength [39].

The non-zero state of residual thermal stresses at low temperatures is the underlying cause of micro cracking in composites and these microcracks propagate results in transverse cracks. When the transverse crack develops further, the crack deflects through the interface between layers and delamination initiates. The delaminations connect the microcraks in adjacent layers and provide leakage paths. The combined cryogenic and elevated temperature thermal cycle produces substantially greater amounts of damage in polymer composites. Thermal shock may often result in intense thermal stresses in the structure during service periods around cracks and other kinds of common manufacturing defects of FRP composite. This may modify the local stress threshold required for interfacial de-bonding. It quite possibly leads to the premature nucleation of delamination failure [48]. At low temperatures the polymer matrices become brittle and do not allow relaxation of residual stress or stress concentration to take place for which the chain movement is restricted which is the cause of less depression of T_g during cryogenic conditioning of the composite sample [58]. Low temperature conditioning improves the strengthening phenomenon due to mechanical keying at the fibre-matrix interface and at room temperature and high temperature act as a softening agent [59]. There are two types of thermal shocks. Low to high temperature (temperature below zero degree to temperature above room temperature) is known as up-thermal shock. In the similar way, the reverse is known as down-thermal shock.

2.8.1 EFFECT OF UP-THERMAL AND DOWN-THERMAL SHOCK ON E-GLASS/EPOXY COMPOSITE:

Ray, B.C. [60] exposed some E-Glass/Epoxy composite samples to -20^0C for 5, 10, 15, 20 minutes and then immediately to $+50^0$C for 5, 10, 15, 20 minutes and some of samples in reverse order i.e. $+50^0$C for 5,10,15,20 minutes to -20^0C for 5, 10, 15, 20 minutes. This literature indicates no such noticeable change observed in ILSS value for (lower and higher) crosshead speeds for up-thermal shock. The weakening effect of thermal shock is neutralized by the strengthening effect of post-curing phenomena at up-thermal shock.

The thermal conditioning results in post curing strengthening effect. Residual stresses are also built-up because of thermal expansion mismatch between the fiber and epoxy matrix. These misfit strains can result in de-bonding effects at the fiber/matrix interface. Another source of residual stress is the differential thermal contraction during sudden cooling from 50^0C temperature to -20^0C temperature. The cryogenic conditioning causes differential contraction and increases the resistance to de-bonding by mechanical keying factor. The characteristic of the interfacial adhesion is strongly influenced by the presence of residual stresses. However, some of the stresses developed by differential expansion/contraction are relaxed by viscoelastic flow or creep in the polymer matrix.

The slight improvement in ILSS (inter laminar shear strength) is observed for lesser conditioning time of down-thermal shock. A marked development of mechanical locking arises at the fiber/matrix interface due to down thermal shock. The mechanical locking may have been dominating over the weakening effect of thermal shock for shorter conditioning time as reported by Ray,B.C. The cryogenic conditioning causes differential contraction and may increases the resistance to de-bonding by better adhesion at the interface. The longer conditioning time for down thermal shock may result in large misfit strain at the interface. Difference in thermal expansion co-efficients of the fiber and matrix result in the development of misfit strain at the fiber/resin interface. The cracklings are observed in SEM photographs of the thermally shocked and thermally conditioned at down ward temperature for greater conditions [39, 60].

2.9 A BIRD'S EYE VIEW ON LITERATURE SURVEY:

TABLE: 2.1

Sl. No.	Authors	Summery
1	*Das,B; Sahu, S.K.; Ray, B.C.; "Effects of Matrix types and Loading speed on the failure behaviour of FRP Composite" ISTAM 2004, NIT, Rourkela, India, Dec 27-30, p24-32*	There has been a tremendous achievement in the science and technology of composite material in recent times.
2	*Boukhoulda, B.F.; Adda-Bedia, E.; Madani, K; "The effect of fiber orientation angle in composite materials on moisture absorption and material degradation after hygrothermal ageing" Composite Structures 74(2006) 406-418*	Composites are used because of their low mass and exceptional performance. FRP structures in general work in more or less aggressive environment, i.e. temperature, humidity, corrosive environment, chemical exposition. An increase in temperature significantly accelerates the moisture diffusion.
3	*Noton, R. Bryan ; "Engineering Applications of Composites" New York, Academic Press, 1974, Composite Materials, Vol -3*	A composite is a structural material that consists of two or more combined constituents of a macroscopic level. These constituents are not soluble in each other.
4	*Hull, D; Clyne, T.W. ; "Introduction to Composite Materials" Cambridge Solid State Science Series, 2nd Edition, 1996, ISBN 0-521-38855-4*	The property enhancement being sought by the introduction of reinforcement is often less pronounced than for polymers with improvement in high temperature performance or tribological properties often of interest. It is important to consider the properties like stiffness, strength and toughness and exhibited by the potential constituents.
5	*Ray, B.C.; "Effects of crosshead velocity and sub-zero temperature on mechanical behaviour of hygrothermally conditioned glass fiber reinforced epoxy composite" Materials Science and Engineering A, Vol -379, Iss1-2,(2004),p39-44*	The major benefit of the composite is their low density, excellent durations, higher specific strength and stiffness, superior corrosion resistance, improved fatigue properties, life cycle cost reduction and design flexibility. The more deleterious effect of freezing treatment is irreversible in nature.

6	*Berketis, K.S.; Tzetzis, D; Hogg, P.J.; "The Influence of long term water immersion ageing on impact damage behaviour and residual compression strength of glass fiber reinforced polymer (GFRP)" Materials and Design 29(2008) 1300-131*	The most important drawback of the composite is their susceptibility to out of plane impact damage such as that imparted by the accidental fall of a tool.
7	*Fundamentals of Metal Matrix Composite, copyright 1993, by Buffer Worth Neinemann*	Some of typical applications of MMCs include their use in fabrication of satellite, missile, helicopter, various types of aerospace and automotive applications.
8	*Huang, Ji-Hua; Dong, Yue-Ling; Wan, Y; Zhao, Xing-Ke; Zhang, H; "Investigation on reactive diffusion bonding of SiCp/6063 MMC by using mixed powders as interlayers" Journal of Material Processing Tecnology, Vol-190, Iss1-3(2007) 312-316*	Aluminium alloy (6063) reinforced with SiCp mainly used in automotive industry.
9	*Mathews, F.L.; Rawlings, R.D.; "Composite Materials: Engineering and Science" 1st Edition 1994, Chapman and Hall publication*	In PMCs the polymers are used as matrix matyerials in the greatest diversity of composite applications, as well as the largest quantities in light of their property and ease of fabrication.
10	*Kelly, A; Zweben, C; " Comprehensive Composite Materials" Vol -2: Polymer Matrix Composite- Chapter 2.01: Epoxy Resins, 2000, ELSEVIER*	In many cases, GRPs are used for a combination of the properties which with the flexibility and ease of processing can lead to unique design solution. Two important advantages of epoxy resin over unsaturated polyster resin are: first, they be partially cured and stored in that state, and second they exhibit low shrinkage during cure.
11	*Callister, D. William ; "Materials Science and Engineering: An Introduction" John Wiley & Sons, 1999 (5th Edition)*	Today glass-reinforced polymers are still by far the most used composite material in terms of volume with the exception of concrete.

12	*Kumar, M. Surendra; Sharma, N; Ray, B.C.; "Structural Integrity of Glass/polyster composites at Liquid Nitrogen Temperature" Journal of Reinforced Plastics and Composites, vol-28, Iss-11,(2009) 1297-1304*	In cold condition, high residual stresses can build up within the fibrous composite materials due to different coefficients of thermal expansion of the fiber and the matrix at low temperature experiences embrittlement which can also affects the property of the composite.
13	*Causin, V; Marega, C; Marigo, A; "When Polymers fail: A case report on a defective epoxy resin flooring" Engineering Failure Analysis 14(2007)1394-1400*	Due to qualities such as versatility, low cost and light weight, polymers are increasingly used in many industries to substitute metals and ceramics.
14	*Kumar, M. Surendra; Ray, B.C.; "Mechanical behaviour of FRP composite at low temperature" 2nd International Conference on Recent Advances in Composite Materials (ICRACM-2007), New Delhi, India*	Recently one area identified as potential source for significant weight reduction in the replacement of traditional metallic cryogenic fuel tanks with advanced polymer matrix composite (PMC) tanks.
15	*Chaudhuri, R.A.; Balaraman, K.; " A novel method for fabrication of fiber reinforced plastic laminated plates" Composite Structures 77 (2007) 160-170*	FRP plates, symmetrically as well as asymmetrically laminated, are widely employed in a variety of industrial applications.
16	*Sogerstrom, S; Ruyter, I.E.; "Effect of thermal cycling on flexural properties of carbon-graphite fiber reinforced polymers" Dent Mater (2009), doi: 10:1016/j.dental.2008.12.007*	The mechanical properties of fiber reinforced composites are dependent on factors such as fiber type and quantity, the adhesion between matrix and fibers, the polymerization shrinkage of the resin and the individual properties of fibers and the matrix.
17	*Mohanty, U.K.; Ray, B.C.; Sethy, S; "Mechanical behaviour of Freeze-Thaw loaded fibrous polymeric composites" COMP 2007 – 038, 6th International Symposium on Advanced Composite Technologies, 2007, Corfu, Greece*	The inclusion of glass fiber which is relatively less costly compared to carbon fiber also reduces the overall cost of the hybrid composite.

18	*Gu,w; Wu, H.F.; Kampe, S.L.; Lu, G.Q.; "Volume fraction effects on Interfacial adhesion strength of glass-fiber reinforced polymer composites" Materials Science and Engineering A 277(2000) 237-243*	With increasing applications of fiber reinforced composite materials more and more knowledge is needed to get a better understanding of the materials which can lead to different mechanical properties of the materials.
19	*Kawaguchi, T; Pearson, Raymond A; "The Moisture effect on the fatigue crack growth of glass particle and fiber reinforced epoxies with strong and weak bonding conditions, Part – I, Macroscopic Fatigue crack propagation behaviour" Composite Science and Technology 64(2004)1981-1989*	The fatigue crack propagation properties of glass/epoxy composites importance since such composites are often used for engineering composites.
20	*Kelly, A; Zweben, C; "Comprehensive Composite Materials" Vol-2, Polymer Matrix Composites, Chapter – 2.16, Composite Processing and Manufacturing, Ramesh Talreja, Jan-Andrsf, 2000 (ELSEIVIER)*	GFRPs are used in aerospace, transport and other industry like leisure, building and marine industries.
21	*Kelly, A; Zweben, C; "Comprehensive Composite Materials" Vol-2, Plolymer Matrix Composites, Chapter – 1.08, David. W. Dwight, "Glass Fiber Reinfocements" 2000 (ELSEIVIER)*	Today over 95% of commercial reinforcement glass fibers are made from E-type.
22	*Olmos, D; Moron, R.L.; Benito, J.G.; "The nature of glass fiber surface and its effect in the water absorption of glass fiber/epoxy composites. The use of fluorescence to obtain information at the interface" Composite Science and Technology 66(2006)2758-2768*	The moisture absorption M(t) can be determined from the weight gain of the specimen as function of time.

23	*Ray, P.K.; Bhusan, A; Bera, T; Mohanty, U; Vadhera, S; Ray, B.C.; "Mechanical behaviour of Hygrothermally conditioned FRP Composites after Thermal Spikes" Proceedings of Emerging Trends in Structural Mechanics and Composites, 2003, p322-332*	Environmental exposure most often lead to matrix degradation, fiber-matrix debonding and delaminations. In the recent years the GRPs specially glass/epoxy composites are widely applied in several civil engineering applications.
24	*d'Almeida, J.R.M.; de Almeida, R.C.; de Lima, W.R.; "Effect of water absorption of the mechanical behaviour of fiber glass pipes used for off shore service waters" Composite Structures 83(2008) 221-225*	One can also cite the lower density and hence weight savings on the final structure and corrosion resistance of resin composites as the other advantages over steel pipes. There are many degradative effect like plasticization of the polymeric matrix, reduction in T_g, swelling affects the fiber matrix interfacial strength.
25	*Kajorncheappunngam, S; Gupta, R.K.; Ganga Rao, Hota, V.S.; "Effects of Ageing Environment on Degradation of Glass-Reinforced Epoxy" Journal of Com;posites for Construction, Vol-6,(2002) 61-69*	It is possible that the presence of moisture in the composite whether by itself or in combination with other chemicals, can initiate undesirable structural changes Within the fiber reinforcement and the matrix or the interface, and this can potentially reduce the durability of the GFRP.
26	*Kelly, A; Zweben, C; "Comprehensive Composite Materials" Vol-1: Fiber Reinforcements and General Theory of Composites, Volume Editor Tsu-Wei Chou, 2000 (ELSEIVIER)*	Glassy materials have no crystallinity or long range order, i.e. they are amourphous. All glass fibers used in GFRP are silicates. In these glasses silica forms a three dimensional network of Si-O bond from the fundamental block of $[SiO_4]^{-4}$ tetrahedral.
27	*Lee, Stuart M.; "Hand Book of Composite Reinforcements" 1993, VCH Publishers, 10th Edition*	The hydrolytic stability of glass-reinforced composites is markedly improved by treatment of the glass with a dilute solution at an organo-functional silane. This operation ia regarded as sizing.
28	*Plonka, R; Mader, E; Gao, S.L.; Bellmann, C; Dutschk, V; Zhandarov, S; "Adhesion of epoxy/glass fiber composites influenced by ageing effects on sizing" Composites: Part A*	Water at the interface of glass fiber and epoxy resin causes replacement of covalent bonds between the siloxane backbones of the sizing material on the glass surface with strong hydrogen bonds between the glass surface, water molecules and the network of silane coupling agents.

	35(2004)1207-1216	
29	*Tautanji Houssam A.; Gomez, W; "Durability characteristics of concrete beams externally bonded with FRP composite sheets" cement and concrete composites 19 (1997) 351-358*	Fiber composites offer unique advantages for solving many civil engineering problems in areas where conventional materials fail to provide satisfactory service life.
30	*Ray, B.C.; "Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites' Journal of Colloid and Interface Science 298(2006) 111-117*	PMCs absorb moisture when these composites are susceptible to heat and moisture when operating in changing environmental conditions. The presence of moisture and the stresses associated with moisture-induced expansion may lower the damage tolerance and structural durability.
31	*Ray, B.C.; Hasan, S.T.; Clegg, D.W.; "Effect of thermal shock on modulus of thermally and cryogenically conditioned Kevler/Polyster composites" Journal of Materials Science Letters, Vol 22, Iss 3, (2003) P 203-204*	Brittle thermoset resins such as unmodified epoxy and polyster, may undergo only a limited extent of deformation prior to failure.
32	*Sutherland, L.S.; Soares, C. Guedes; "Effect of laminate thickness and of matrix resin on the impact of low-fiber volume, woven roving E-Glass composites" Composite Science and Technology 64(2004)1691-1700*	Laminated fiber reinforced composite materials are widely used in the marine industry due to their good environmental resistance, the ease with which they may be formed into complex shapes, and also their high specific strength and stiffness.
33	*Tsai, Y.I.; Bosze, E.J.; Barjasteh, E.; Nutt, S.R.; "Influence of hygrothermal environment on thermal and mechanical properties of carbon fiber/fiber glass hybrid composites" Composite Science and Technology 69(2009) 432-437*	The effects of environmental exposure of fiber-reinforced polymer composites (FRPC) and long term retention of properties are significant concerns for much applications where the service life can span several decades and little or no maintenance is expected.
34	*Patel, S.R.; Case, S.W.; "Durability of hygrothermally aged graphite/epoxy woven composite under combined hygrothermal conditions" International*	Impact of environmental factors such as temperature and humidity on composite materials behaviour is at significant concern for the aircraft industry since storage and operating conditions vary considerably and can add to

	Journal of Fatigue 24(2002) 1295-1301	the wear and tear of structural components.
35	*Kootsookos, A; Burchill, P.J.; "The effect of the degree of cure on the corrosion resistance on vinyl ester/glass fiber composites" Composites: Part A 35(2004) 501-508*	The applications where corrosive environments are experienced by the material, further degradation of the mechanical properties can occur.
36	*Tsenoglou, C.J.; Burchill, P.J.; "The effect of degree of cure on the corrosion resistance on vvinyl ester glass fiber composites" Composites; Part A 35(2004) 501-508*	Composites with common structural polymer matrices often absorb moisture and this has preferred effects in their mechanical, thermal, dielectric and barrier property performance.
37	*Shrama, N; Kumar, M. Surendra; Ray, B.C.; "Study the effect of hygrothermal ageing on glass/epoxy micro composites by FTIR- Imaging and Alternating DSC Techniques" Journal of Reinforced Plastics and Composites, Vol-27, Iss15, (2008),1625-1634*	The nature and order of degradation by complex and active environments need to be critically investigated to expand the acceptability of such type of PMCs like E-Glass/Epoxy composite.
38	*Sala, G; "Composite degradation due to fluid absorption" Composites: Part B 31(2000) 357-373*	The principal types of damage that occur to composites are inter laminar crackings, inter laminar delaminations, fiber breakage, fiber-matrix interface failure and fiber pull-out.
39	*Ray, B.C.; "Thermal shock on interfacial adhesion of thermally conditioned glass fiber/epoxy composites" Materials Letters 58(2004) 2175-2177*	Thermal expansion coefficients of polymers are substantially greater compared to metals and ceramics. This is why failure of the bond between fiber and resin (contd...) occurs under the influence of temperature gradient.
40	*Kelly, A; Zweben, C; "Comprehensive Composite Materials" Vol-2, Plolymer Matrix Composites, Effects of fluids on Polymeric Composites: A Review by Y.Jack Weitsmsn, 2000 (ELSEIVIER)*	The complexity in the polymeric composites is compounded by the ingress of fluids of many kinds, which interact differently with the polymer, the fiber and the interface within the composite.

41	*Diamant, Y; Marom, G; Broutman, L.J.; "The effect of network structure on moisture absorption of epoxy resins" Journal of Applied Polymer Science 26(1981),3015-3025*	The presence of holes is determined by the polymer structure and morphology reflected in its degree of crystallinity, crosslinking density, molecular chain stiffness and ability to closely pack in amorphous state.
42	*Springer, G.S.; "Environmental effects on epoxy matrix composites" Composite Materials: Testing and Design (5th Conference)ASTM STP 674, s.w. Tsai, Ed., American Society for Testing and Materials, 1976,p291-312*	The mass diffusion coefficient D may depend also on the concentration and the stress level inside the material.
43	*Ray, B.C.; Biswas, A; Sinha, P.K.; " Hygrothermal effects on the mechanical behaviour of fiber reinforced polymeric composites" Metals Materials and Process: 3 (1991) 99-108*	Epoxy resin absorbs water from the atmosphere with the surface layer reaching equilibrium with surrounding environment very quickly followed by diffusion of the water into all the material. The water absorbed is not usually in the liquid form but consists of molecules or group of molecules.
44	*K. Assbee, "Fundamental principle of fiber reinforced composites", Technomic Publishing Co., Lancaster (1993), p323.*	A concentration driven osmotic process is responsible for moisture absorption into the matrix of the composite under hydrothermal ageing condition.
45	*KHG Assbee, R. Wyatt, Water damage in glass fiber/resin composites, proceedings of the Royal society A 1969; 312:523*	Assbee et.al. proposed osmosis of the interface by alkali metal oxides leaching from E-glass in the presence of moisture.
46	*Luo, S; Leisen, J; Wong, C.P.; " Study on mobility of water and polymer chain in Epoxy: Its influence on Adhesion" Journal of applied polymer science, 85(2002) 1-8*	Moisture transport in polymers is related to molecular sized holes (nano voids) within the polymer matrix and to the polymer matrix-water affinity.
47	*Mishra, G; Mohapatra, S.R.; Behera, P.R.; Dash, B; Mohanty, U.K.; Ray, B.C.; "Environmental stability of GFRP laminated composites: An emphasis on mechanical behavior"*	The primary mechanism of moisture pick up by the FRP composites is surface absorption and diffusion through the matrix is given by Fick's second law of diffusion. The rate of moisture desorption is very less in sub ambient region where as the rate is very high in thermal region.

	Aircraft Engineering and Aerospace Technology: An International Journal,, Vol-82 Iss-4,(201,p258-266.	
48	*Abdel-Magid, B; Ziaee, S; Gass, K; Schneider, M; "The combined effects of load, Moisture and temperature on the properties of E-Glass/epoxy composites" Composite Structures 71(2005) 320-326*	The presence of water in the matrix and at the interface in conjunction with the axial load increases, the effective contact area/region between fiber and matrix in which strong physical interaction can create adhesion between fiber and matrix.
49	*Ray, B.C.; "Effects of changing sea water temperature on Mechanical properties of GRP composites" Polymers and Polymer Composites Vol-15(2006), Iss-1, p1-6*	Inter laminar shear strength ILSS is determined by the formula $\text{ILSS} = 0.75\, p_b / bt$, Where p_b=breaking load b= width of the specimen t= thickness of the specimen
50	*Bond, I; Hucker, M; Weaver, P; Bley, S; Haq, S; "Mechanical behaviour of circular and triangular glass fibers and their composites" Composite Science and Technology 62(2002 1051-1061*	Composite laminates can easily attain the design requirements for tensile load with a minimum number of plies are then often not sufficiently thick to provide rigidity in flexure or buckling problem in compression.
51	*Adams, R.D.; Singh, M.M.; "Low temperature transitions in fiber reinforced polymers" Composite Part A 32(2001) 797-814*	The transition from a glassy to rubbery state is accompanied by a rapid fall in modulus, and a peak in the damping or loss factor of the material.
52	*Karbhari, V; Wang, Q; "Multi-frequency dynamic mechanical thermal analysis of moisture uptake in E-Glass/vinyl ester composites" Composite Part B 35(2004) 299-304*	The increasing use of low-cost polymer matrix composites processed under ambient and moderate temperature regimes for applications requiring long service life increases the requirements for a comprehensive understanding of their response as a function of exposure environment and a time.
53	*Hung, G; Yalizis, A; Frant Ziskonis, George, N; "Hygrothermal degradation in glass/epoxy-evaluation via stress wave factors"*	The long term mechanical reliability and safety of composite material structure depends on the environment to which a structure is exposed to.

	Composite Structures 30(1995) 407-417	
54	*Vauthier, E; Abry, J.C.; Bailliez, T; Chateuminois, A; "Interaction between hygrothermal ageing and fatigue damage in unidirectional glass/epoxy composites" Composite Science and Technology 58(1998) 687-692*	It is also widely acknowledged that hygrothermal ageing may significantly weaken the material constituents.
55	*Sharma, Neeti; Ray, B C; "Assessment of Small Interactions and Structural Gradient at the Interface of Glass and Carbon Fibers Epoxy and Micro-composites by FTIR-Imaging and DSC Techniques" Proceedings of the Conference on Emerging Trends in Engineering Materials, 1-3 Feb 2007, Patiala*	When FRP composites are exposed to hygrothermal environment for longer period, the T_g usually decreases and therefore, the service temperature of the material changes
56	*Gellert, E.P.; Turley, D.M.; "Sea water immersion ageing of glass fiber reinforced polymer laminates for marine applications" Composite Part A Vol-30, Iss-11 (1999), p1259-1265*	Applications of glass fiber/epoxy composites including marine components such as masts, submarine control surfaces, transmission shafts and propellers. Sea water immersion may result in fiber related mechanisms for transport of moisture into the composite body. These mechanisms include transport of moisture along the interface and/or continuing diffusion through the matrix with accumulation of the fiber.
57	*Wood ,Catherine A. ; Bradley, Walter L. ; "Determination of the Effect of Sea water on the Interfacial Strength of an Interlayer E-Glass/ Graphite/ Epoxy Composite by In Situ observation of transverse cracking in an Environmental SEM" Composites Science and Technology 57 (1997) 1033-1043*	A drawback to using composites in offshore applications is the lack of information concerning the long-term effects of sea water on composites. There have been a few studies in which specimens were aged under conditions similar to that of the ocean environment, and even fewer studies to investigate the long-term effects of such exposure.

58	*Costa M L; Muller de Almeida S. F.; Rezende M. C; "Hygrothermal Effects on Dynamic Mechanical Analysis and Fracture Behavior of Polymeric Composites." Journal of Materials Research. Volume 8, No. 3, (2005): p. 335-340*	At low temperatures the polymer matrices become brittle and do not allow relaxation of residual stress or stress concentration to take place for which the chain movement is restricted which is the cause of less depression of T_g during cryogenic conditioning of the composite sample
59	*Ray B C, "Adhesion of Glass/Epoxy Composites Influenced by Thermal and Cryogenic Environments." Journal of Applied Polymer Science. Volume 102, No. 2, (2006): p.1943-1949.*	Low temperature conditioning improves the strengthening phenomenon due to mechanical keying at the fibre-matrix interface and at room temperature and high temperatureact as a softening agent.
60	*Ray, B.C. "Effects of Thermal and Cryogenic Conditionings on Mechanical Behavior of Thermally Shocked Glass Fiber/Epoxy Composites" Journal of reinforced plastics and composites, vol 24,no 7, 2007, P 713-717*	It is therefore necessary to examine what really happens at the interface by thermal shock treatment. The fiber and matrix interactions are likely to be greater in woven fabric composites as compared to composite made up of unidirectional fibers.

2.10 Conclusions

The works of several workers have been thoroughly studied and their conclusive findings have been recorded concerning the effect of different moist environment and thermal shock on E-glass fiber/epoxy composite separately. At the end of this chapter the conclusive findings of the investigators have been presented in a tabular form. Here it is imperative to investigate about the effect of various moisture environment (hydrothermal, hygrothermal and sea water immersion) coupled with thermal shock (up-thermal and down-thermal shock) on such type of composites.

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Chapter-3

EXPERIMENTAL

EXPERIMENTAL

3.1. Introduction

This chapter describes the experimental procedure as adopted in the present project-work. The Equipment/Instruments utilized to carry out the experiments are listed in a tabular form indicating their specific use in the project along with their specifications and particulars in details. All the experimental procedures are given in a flow sheet.

A detailed report is also provided on the raw materials used for fabrication of FRP-test samples. This chapter encloses a clear cut description of the detailed step wise methods implemented for fabrication of the test specimens, taking fix weight of the samples by heating process, the different moisture treatment, the thermal shock treatment with varying time periods. The characterization of the sample including the mechanical testing by 3-point bend test (ILSS determination), generation of the micrographs through scanning electron microscopy for micrograph analysis and determination of glass transition temperature of specimens in required situations. The photographs of the Equipment/Instruments used in the present work are also presented.

3.2 EQUIPMENT / INSTRUMENTS USED IN THE PRESENT INVESTIGATION

Table: 3.1 presents a detailed list of the Equipment/Instruments used in the present investigations along with their specific use in the experiments conducted and their detailed specifications. Table: 3.1 is presented in the next page.

3.3 MATERIALS USED

- **Epoxy Resin**

Specification - Araldide LY-556 based on Bisphenol-A

- **Hardener**

Specification - HY- 951 an aliphatic primary amine (Ciba-Geigy)

- **Glass Fiber**

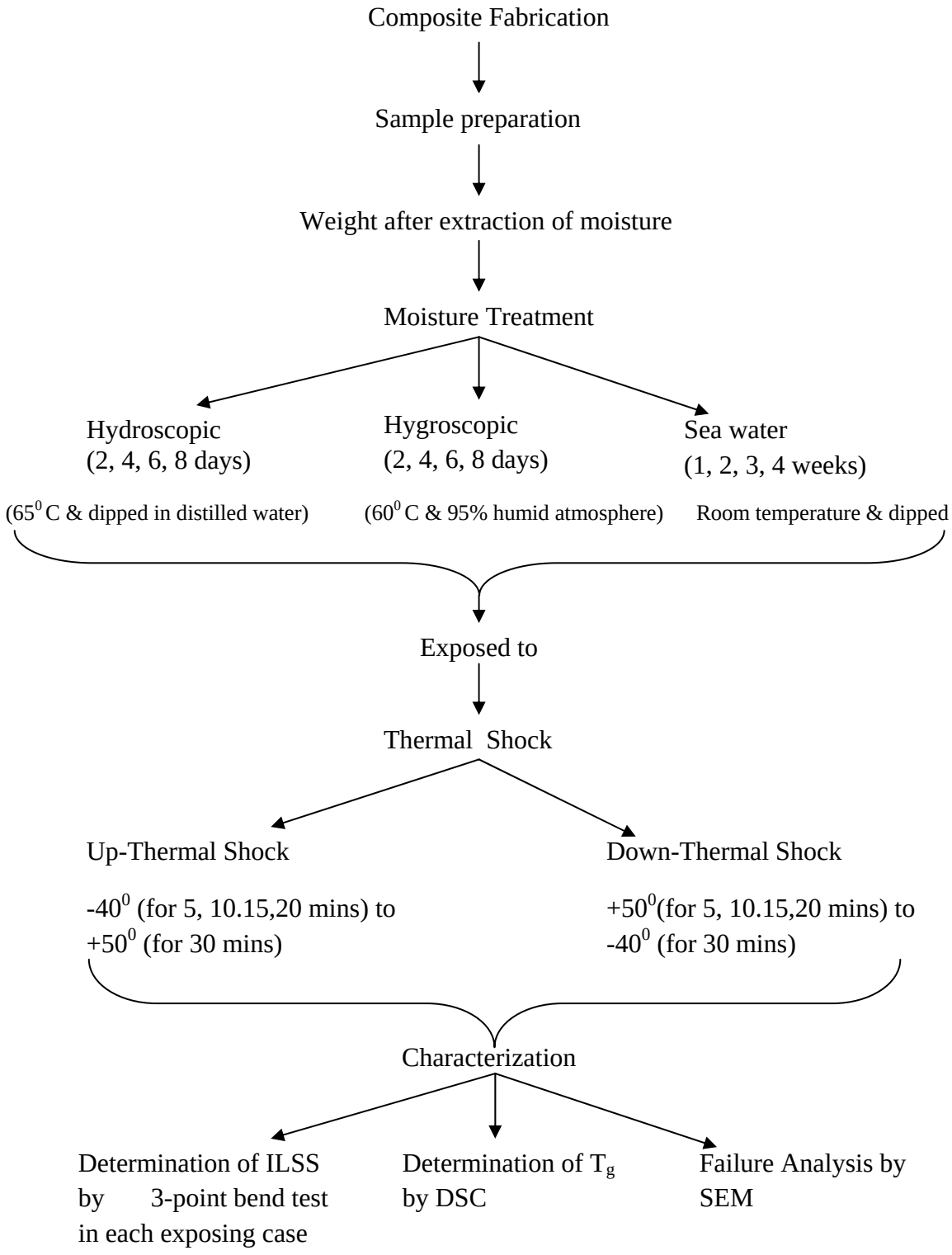
  Woven glass fibers are used for fabricating the layered composites.

  Thermoplastic films are used for easy detachment of composite after complete curing of the composite.

TABLE: 3.1 (LIST OF THE EQUIPMENT/INSTRUMENTS USED)

Sl.No.	EQUIPMENT / INSTRUMENT	SPECIFICATIONS	USE IN THE PRESENT INVESTIGATION
1.	Diamond Cutter	High Speed	For sample preparation in required dimension 50 mm (length) x 12 mm (breadth)
2.	Slide Caliper (Electronic)	Measuring up to 3rd decimal of accuracy.	For measuring the sample length, width and thickness
3	Hygrothermal Chamber Microprocessor controlled Brabender climatic chamber	Temperature Range: Room Temp to 60^0C Humidiry range: Up to 95% Relative Humidity	For Hygrothermal exposure (60^0C+95% R.H.)
4.	DSC (Differential scanning calorimeter)	Mettler-Toledo 821 with intra cooler	Determination of glass transition temperature
5.	Electric Oven	Range- 30^0C to 300^0C	For exposing the samples to a thermal shock at + 50^0C, an elevated temp.
6.	Cryogenic Chamber	Make –S.D. Scientific Industries Ultra Low Chamber Range: +50^0C to – 80^0C	For exposing the samples to a thermal shock at – 40^0C, sub ambient temperature.
7.	Instron-1195	Make-Instron Ltd. Model-1195 Range-0.1N to 100KN	For determination of Inter Laminar Shear Strength (ILSS) by adopting 3-Point Bend Test method.
8.	Scanning Electron Microscope (SEM)	Make-JEOL Type-JSM-6480LV	For obtaining the micrographs of the composites.

3.4 EXPERIMENTAL FLOW SHEET



3.5 FABRICATION OF E-GLASS/EPOXY COMPOSITE

HAND LAY-UP METHOD

The layered based composite was fabricated using the conventional hand Lay-up method shown in figure: 3.1. In hand lay-up method the woven E-glass fiber is put down to line a mould previously treated with release agent to prevent sticking and a gel coat to give a decorative or protective surface. The liquid epoxy resin (Araldite LY556) is mixed with a curing agent/hardener (diamine HY951) and applied with a brush or roller taking care to work it into the glass fiber. The prime consideration is the viscosity and the working time of the resin. The main disadvantages of this method are the low reinforcement content of about 30 vol% and the difficulty in removing all the trapped air. An eighteen layered structure was formed. The fiber and the matrix were taken in the ratio of 50:50. The layered structure was allowed to harden on cure. It was cured at room temperature for 48 hours so that the matrix completely seeps in and become dry.

3.6 SAMPLE PREPARATION

CUTTING OF LAMINATES INTO SAMPLES OF DESIRED DIMENSIONS

After curing, the laminate was cut into the required size for 3-point bend (Short-Beam Shear) test by diamond cutter. A diamond cutter was used to cut each laminate into smaller pieces, each having dimensions of 50 mm x 12 mm and thickness same as that of the laminate. This was done in accordance with ASTM standards. The length of the specimen should be greater than 10 times the thickness and maximum width given as D+2t, where D is 10 and t is the thickness of the composite according to ASTM D 2344-84 (1989) standard.

3.7 WEIGHT AFTER EXTRACTION OF MOISTURE

Before exposing the specimens to any sort of environment, moisture should be removed completely. Samples were heated up to 55^0C-60^0C in an electric woven. The weight of the samples was taken after heating. This process was continued until there is no change in the weight or till the specimens have constant weight. Here the moisture which entrapped in to the composite during curing and cutting by diamond cutter was fully removed.

3.8 MOISTURE TREATMENT

3.8.1 HYDROTHERMAL TREATMENT:

An electric woven is used for hydrothermal treatment. The electric woven is maintained for 65^0C early before the exposing. A group of samples required for thermal shock immersed in distilled water in bikers (indication given in first, second, third and fourth biker as *2, 4, 6 and 8 days hydrothermal treatment respectively*). The bikers are kept in electric woven which maintained for 65^0C early before the exposing. The groups of samples required for different thermal shocks are exposed to 2, 4, 6 and 8 days. Water level checked within a regular interval (4 hours). After exposing for 2, 4, 6 and 8 days, the samples were dried by tissue paper and weighed in electronic balance. The weights of the exposed samples were noted. Then the samples are wrapped by aluminum foil and kept in deciccator to avoid further moisture absorption. The percentage of moisture gain was calculated by the formula given in Chapter-2 (equation number -6, section-2.7.1.3)

3.8.2 HYGROTHERMAL TREATMENT:

A humidity chamber (figure: 3.2) was used for hygrothermal treatment. Once the chamber is switched on sufficient time gap was allowed till the required humidity and temperature was attained (R.H=95%, TEMP=60^0C). The hygrothermal chamber is shown in figure: 3.2. Precautions were taken to maintain the level of distilled water in the tank at the desired level, also the distilled water level for the wet bulb thermometer was kept at appropriate level. The net temperature fluctuation was 0.7^0C, while the humidity fluctuation ranged up to a maximum of 0.4 percent. Then a group of samples (further required for up and down thermal shock) were put into the chamber and subsequently removed after predetermined time periods (2, 4, 6, 8 days). After the hygrothermal treatment was over each specimen is weighed by an electronic balance (corrected up to 4 places of decimal) after wiping the specimens clean using a tissue paper so that no excess moisture remains on the surface. Specimens were then wrapped in aluminum foil so as to avoid moisture loss or moisture pickup. The wrapped samples were kept in deciccator. The percentage moisture uptake was calculated by the expression given in Chapter-2 (equation number - 6) and moisture pick up by the samples are shown by graphs (percentage of moisture absorption vs.

square root of time of exposing) in results and discussions chapter. The hygrothermal chamber is shown in fig: 3.3.

3.8.3 SEA WATER TREATMENT:

A group of samples required for treatment of thermal shock were immersed in sea water (figure: 3.4) in different bikers (indication given in first, second, third and fourth biker as 1, 2, 3 and 4 weeks sea water treatment respectively). After exposing for required durations (1, 2, 3 and 4 weeks), the exposed samples are dried by tissue paper and weighed in electronic balance. The weights of the exposed samples were noted and percentage of moisture gain was calculated. Then the samples were wrapped in aluminum foil and kept in deciccator to avoid further moisture absorption.

3.9 THERMAL SHOCK TREATMENT:

3.9.1 UP-THERMAL SHOCK TREATMENT:

The each group of moisture exposed samples (hydrothermal, hygrothermal and sea water) was exposed to up-thermal shock. The electric woven and cryogenic chamber (deep freezer) were switched on and maintained $+50^0$C and -40^0C respectively before shock treatment. The samples were exposed to up-thermal shock by varying time period of exposing. The shock treatment was given as -40^0C for (5, 10, 15 and 20 minutes) to $+50^0$C for 30 minutes. After each case of exposing the shock treated samples were subjected to 3-point bend test for ILSS (Inter Laminar Shear Strength) determination quickly.

3.9.2 DOWN-THERMAL SHOCK TREATMENT:

The electric woven and cryogenic chamber (deep freezer) were switched on and maintained the desired temperature as in up-Thermal shock. The each group of moisture treated samples was exposed to down thermal shock by varying time period of exposing. The shock treatment was given as $+50^0$C for (5, 10, 15 and 20 minutes) to -40^0C for 30 minutes.

After each case of exposing the shock treated samples were subjected to 3-point bend test for ILSS (Inter Laminar Shear Strength) determination quickly.

The electric woven and cryogenic chamber are shown in figure: 3.5 and figure: 3.6.

3.10 CHARACTRIZATION

3.10.1 3-POINT BEND TEST: (ILSS DETERMINATION):

The shock treated (up and down thermal shock) and moisture treated (hydrothermal, hygrothermal, sea water treated) samples were subjected to 3-point bend test. The INSTRON -1195 was made to be ready for 3-point bend test at the time of shock. The samples were sent to the INSTRON room with proper care in desiccator. The span length was maintained to be 40mm and crosshead velocity 1 mm/sec. For each case of shock treatment 4 samples were taken for bend test. The average ILSS for each case of moisture and shock treatment was listed in tabular form.

ILSS is calculated by the formula given by

$$\text{ILSS} = 0.75\ p_b \big/ bt$$

Where p_b = breaking load (load at rapture in KN)

b = width of the specimen

t = thickness of the specimen.

$$\text{ILSS} = 0.75 \times 1000 \frac{p_b}{bt} \text{ N/mm}^2 \text{ or (MPa)}$$

The INSTRON -1195 is shown in figure: 3.7. The breaking of laminated sample by 3-point bend test is shown in figure: 3.8.

3.10.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

GLASS TRANSITION TEMPERATURE (T_g) DETERMINATION:

The glass transition temperature was measured for up and down thermal shock treated of 8 days hydrothermal, 8 days hygrothermal and 4 weeks sea water treated samples. The T_g variation was investigated in these extreme cases.

The DSC measurements were performed on a Mettler-Toledo 821(figure: 3.9) with intra cooler, using the STAR software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of 10^0 C/min was used. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminum pans were used. The experiments were performed in the temperature range from 30^0C to 150^0C. The first change of slope in the curve determines the T_g.

3.10.3 SCANNING ELECTRON MICROSCOPY:

MICROGRAPH ANALYSIS:

The micrograph taken by SEM for up and down thermal shock treated of 8 days hydrothermal, 8 days hygrothermal and 4 weeks sea water treated samples. The samples were first being loaded on the loading plate and then viewed under SEM to fix the positions of the plate. Vacuum level of the SEM chamber is being adjusted from time to time depending on the requirement. After that the samples were given coating of platinum in order to make them conducting. The SEM is shown in figure: 3.9.

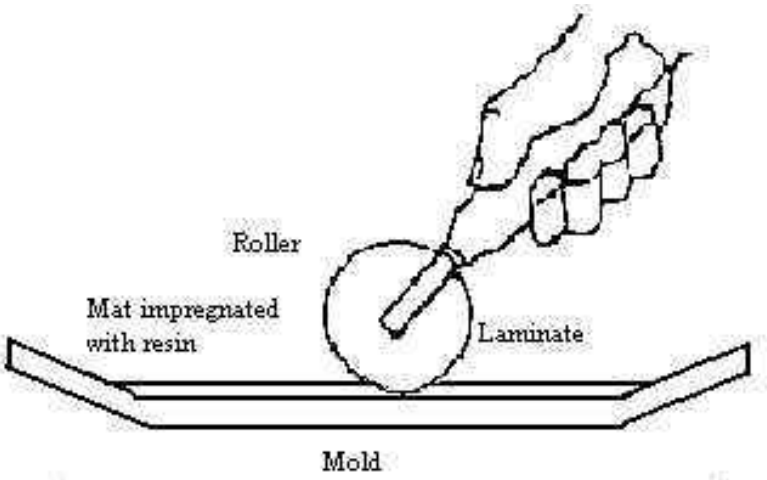


Fig: 3.1 (Hand lay-up method for fabricating laminar composite)

Fig: 3.2 (Humidity Cabinet)

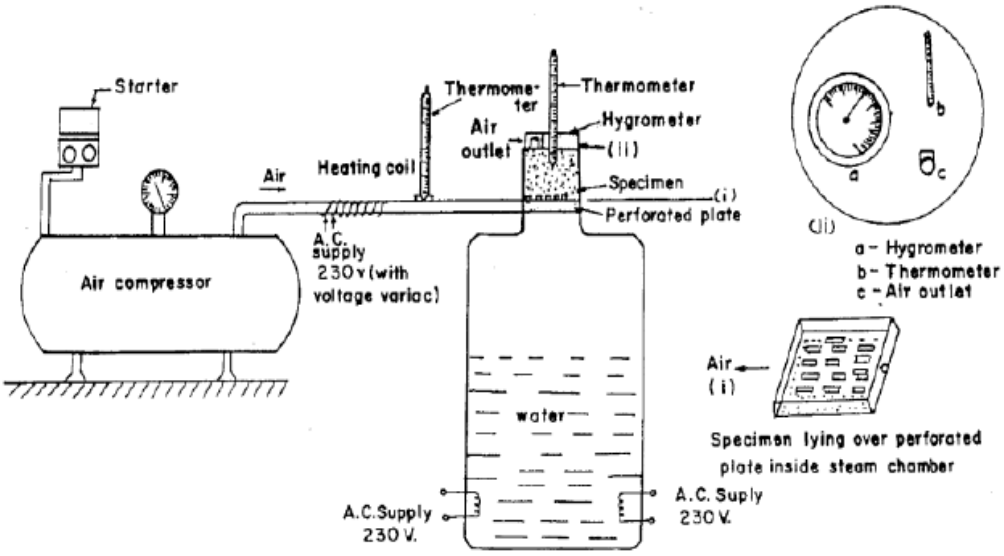


Fig: 3.3 (Schematic diagram of hygrothermal chamber)

Fig: 3.4 (Sea water immersion of glass fiber/epoxy composites for different durations)

Fig: 3.5 (Electric woven)

Fig: 3.6 (Cryogenic Chamber)

Fig: 3.7 (INSTRON-1195 with 3-point bend test set-up)

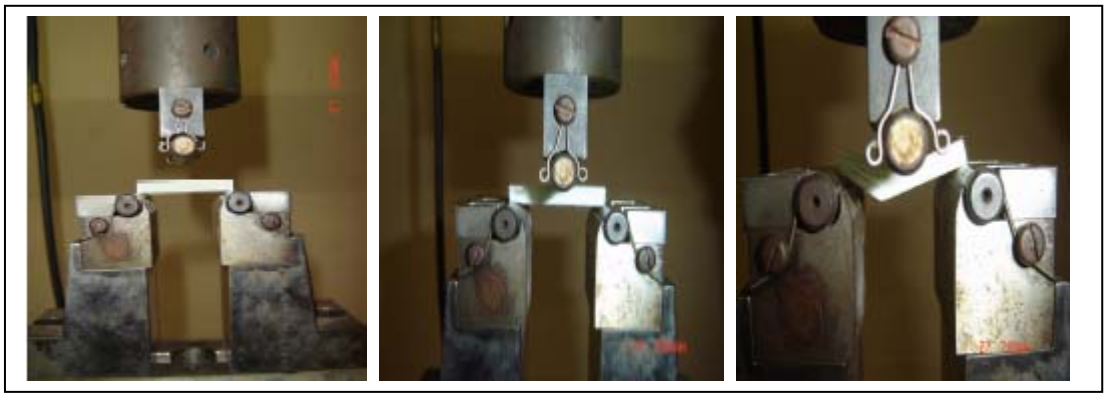


Fig: 3.8 (Breaking of laminated composite by 3-point bend test)

Fig: 3.9 (a) Mettler-Toledo 821 with intra cooler for DSC measurements and (b) Reference-sample chamber

Fig: 3.10 (Scanning Electron Microscope)

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Chapter-4

RESULTS AND DISCUSSIONS

RESULTS & DISCUSSIONS

4.1 MOISTURE ABSORPTION:

Table: 4.1 contains data pertaining to moisture absorption as a function of time when exposed to hygrothermal, hydrothermal and sea water conditioning. The hygroscopic chamber was maintained at 60^0C with 95% R.H. The distilled water bath for hydroscopic exposure was maintained at 65^0C and the immersion in sea water was done at room temperature.

TABLE -4.1 (Moisture absorption as a function of time for hygrothermal hydrothermal and sea water conditioning)

Hygrothermal Exposure 60^0C + 95% R.H.		**Hydrothermal Exposure 65^0C + Dipped in distilled water**		**Sea Water Exposure Room Temperature + Dipped**	
Time in hours	% of Moisture Gain	Time in hours	% of Moisture Gain	Time In hours	% of Moisture Gain
48	0.824383926	48	0.77377787	168	0.359310198
96	0.984082	96	0.801594	336	0.386881678
144	1.104169669	144	0.972317	504	0.779226302
192	1.416792732	192	1.115085	672	0.822181529

The data presented at Table: 4.1 was presented in terms of graphs showing percent of moisture gain plotted against square root of time in hours in Fig no through -4.1, 4.2, and 4.3.

Fig: 4.4 represents all the three curves at one page for the sake of comparison. Also the same data presented in the form of bar diagram in fig: 4.5

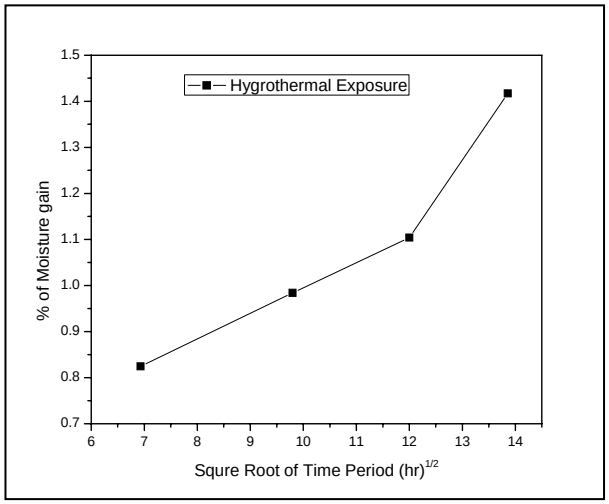

Fig: 4.1 (Percentage of moisture gain for hygrothermally treated sample)

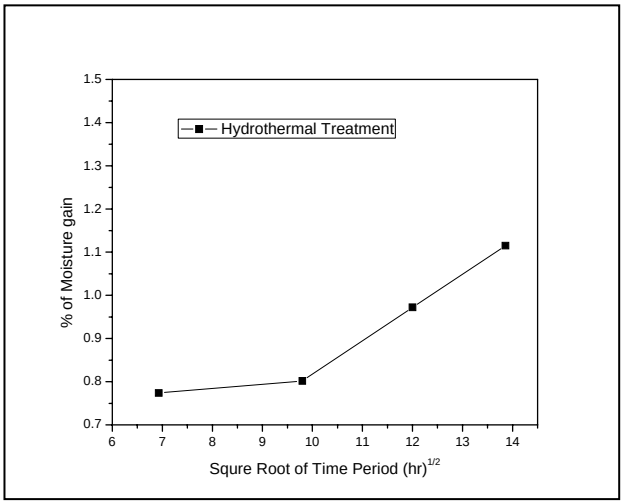

Fig: 4.2 (Percentage of moisture gain for hydrothermally treated sample)

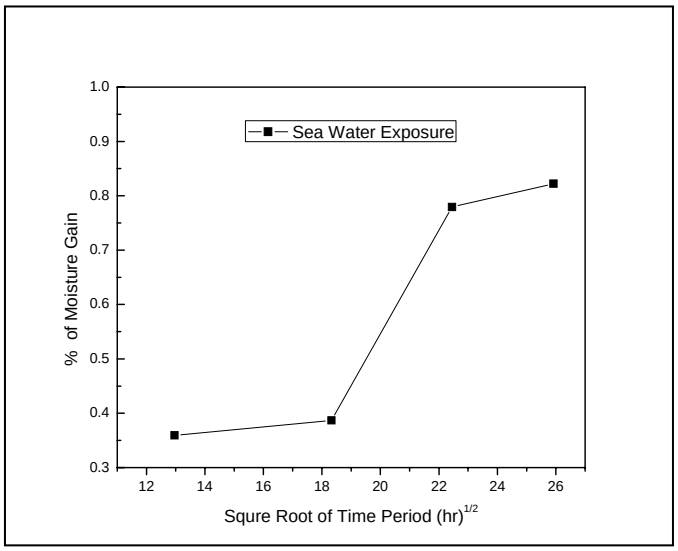

Fig: 4.3 (Percentage of moisture gain for Sea water treated sample)

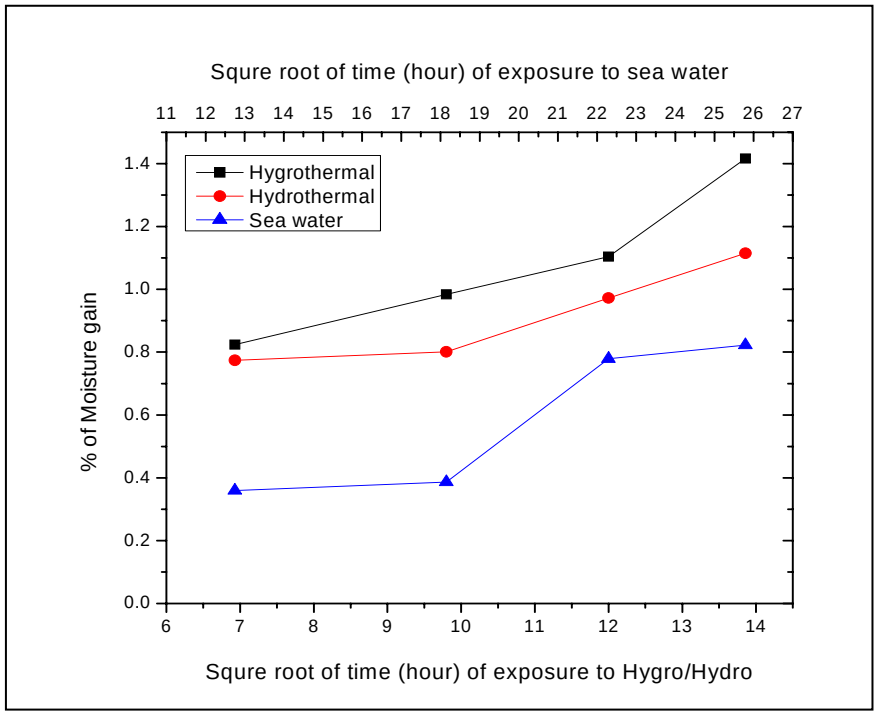

Fig: 4.4 (Percentage of moisture gain for hygrothermally, hydrothermally and sea water treated sample)

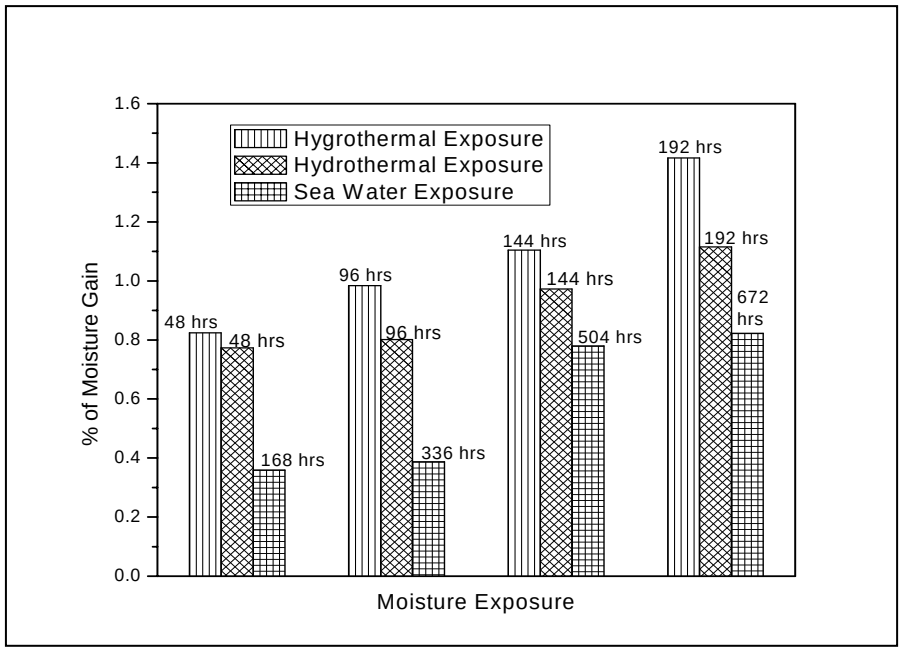

Fig: 4.5 (Percentage of moisture gain for hygrothermally, hydrothermally water treated sample treated sample)

The data reveals the following

(i) In all three cases moisture intake increases with the time of exposure.

(ii) The rate of moisture peak up in the initial stages is the highest in the case of hygroscopic conditioning.

(iii) Both sea water and hydroscopic immersions exhibit similar rates of initial moisture absorption which is lower than that observed in the case of hygroscopic conditioning, sea water immersion resulting in the lowest rate of moisture absorption.

(iv) The total moisture intake is lower in case of hydroscopic conditioning compared to that of hygroscopic conditioning; though in both the cases the exposure time is identical.

(v) In the case of sea water immersion, the total moisture intake is the lowest notwithstanding the fact that, in this case the exposure time is much more than that in the other two cases.

(vi) In all the three cases the weight percent moisture uptake plots show a continuing uptake trend rather than a plateau even after continued exposure to the respective conditioning environments.

Epoxy composite laminates tend to be slightly hygroscopic. They absorb moisture directly from the ambience as a function of temperature and the relative humidity and also when these are immersed directly in water, ordinary or saline. The primary mechanism for moisture peak up by the FRP composite is surface absorption and diffusion through the matrix [42]. It obeys Fick's second law i.e.

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2}$$

Where c = the moisture concentration

x = the thickness coordinate

D_x = the diffusivity of the material, t = the time of exposure.

The driving forces behind the ingress of moisture which involve absorption, diffusion and permeation are the concentration difference of moisture between the two phases. Thus it is evident that the initial absorption of moisture into the composite bodies in all the three cases investigated is concentration dependent and obeys Fick's 2^{nd} law, the absorption of moisture being a direct function of the time of exposure.

Further the absorbed moisture may change the diffusion behavior of the FRP composite by changing the glass transition temperature (T_g), generating cracks due to swelling of the matrix etc. whether the diffusion process is concentration dependent, i.e. Fickian or Non-Fickian i.e. does not only depend upon concentration gradients, depends on the relative rates at which the polymer structure and moisture distribution change. In the initial stages when the polymer structure changes much faster than the moisture concentration, obviously the transport of moisture is concentration dependent and can be adequately described by Fick's law and is termed Fickian. Here the rates of moisture diffusion are much slower than the relaxation process. This is found to be true in all the three cases examined.

Moisture absorption by epoxy composite can result in the formation of concentration gradients through the laminates. These concentration gradients may cause unequal swelling stresses and result in the formation of microcrack.

Fick's law is generally applicable to rubbery polymers but often fails to describe diffusion process in glassy polymers. The glassy polymers may exhibit Non-Fickian or anomalous behavior pertaining to moisture peak up. The transition from glassy to rubbery state occurs at the (T_g) glass transition temperature. The T_g itself depends on the moisture concentration and the absorbed moisture may change the diffusion behavior by changing the T_g.

The experimental data exhibit that after the lapse of certain time period the rate of moisture peak up is much enhanced in all the three cases, notwithstanding the fact that the initial concentration dependent rate of moisture peak up would have been decreased subsequently with the concentration gradients decreasing with time progressively with the ingress of more and more moisture. Here the moisture absorption is anomalous, can't be

explained by the Fick's law and is thus Non-Fickian. This is attributed to the development of microcrack, delamination, debonding etc. between the fiber and the matrix as a result of swelling of the matrix and also to a change in the diffusion behavior by an alternation of the (T_g) glass transition temperature as discussed above. It is only pertinent to mention here that moisture absorption by epoxy composite can result in the formation of concentration gradients through the laminates. These concentration gradients would cause unequal swelling stresses and would result in the formation of microcracks, debonding and delaminations etc. in the composite body.

The moisture absorbed by the composite is not usually in liquid form but consists of molecules or group of molecules linked by hydrogen bonds to the polymer. This explains the highest rate of moisture absorption under hygrothermal conditioning where the ambience is laden with water (H_20) molecules (> 90% relative humidity) as compared to a situation when the specimens are immersed in water whether distilled or saline.

Sea water ageing still remains an uncertain factor [56]. Epoxy resins are permeable to water but impermeable to the ions present in a number of aqueous solution. A concentration driven osmotic process is responsible for moisture absorption into the matrix of the composite under hydrothermal ageing condition [44]. Assbee [44] observes that osmotic pressure is less of a problem in saline solutions than in pure water. Probably the bulky nature of various salts present in sea water with their osmotic effect influence the rate of moisture absorption with time when the composite specimens are immersed in sea water. The net result is an initial lower rate of moisture absorption in the case of sea water immersion as compared to the other two cases as evident from the experimental findings.

Gellert et.al. [56] propose that sea water immersion may result in fiber related mechanisms for transport of moisture into the composite body. These mechanisms include transport of moisture along the interface and/or continuing diffusion through the matrix with accumulation of the fiber. Assbee et.al. [45] have actually illustrated etching on the surface of glass fibers. They have differentiated three glass fiber types on the basis of correlations between alkali content and fiber debonding considered resulting from osmotic pressure.

They proposed osmosis of the interface by alkali metal oxides leaching from E-glass in the presence of moisture. This leaching, they suggested, would form concentrated salt solutions and the concentration gradient would drive further diffusion of water towards the interface.

The above would explain the anomalous nature of moisture ingress in the case of sea water immersion. Thus it can be inferred that moisture ingression into the composite is partly conducted by diffusion involving transport of water molecules into the matrix and in some cases, into the fibers. Water can also diffuse rapidly into the composites along the fiber-matrix interface which is also known as water wicking and represents an accepted mechanism for conveying water to the interior of composites.

The continuing trend of moisture uptake in all the three cases is indicative of supplementary mechanism of moisture intake with lengthening of exposing time, establishing the fact that longer exposures only helped in greater and greater degradation of the composite which assist further moisture uptake delaying the saturation level of moisture uptake by the composite body.

4.2 Inter Laminar Shear Strength without thermal shock

Table: 4.2 contains data pertaining to inter laminar shear strength (ILSS) of hydroscopic, hygroscopic and sea water treated sample as a function of exposing time. The ILSS of as cured sample was found to be 29.75 MPa. The ILSS was measured by INSTRON-1195 adopting 3-point bend test method.

TABLE: 4.2 (ILSS of hydroscopic, hygroscopic and sea water treated sample as a function of time)

Number of **days** for Hydrothermal Exposure **(65^0C+dipped in distilled water)**	ILSS in MPa	Number of **days** for Hygrothermal Exposure **(60^0C+95% R.H.)**	ILSS in MPa	Number of **weeks** for Sea Water Exposure **(Room Temp.+ Dipped)**	ILSS in MPa
2	22.28952425	2	26.13980151	1	29.1013
4	26.73541016	4	27.35629467	2	29.51643
6	26.3495278	6	24.78790522	3	29.9027
8	30.20178584	8	25.86781481	4	25.44418

The data presented at Table: 4.2 was presented in terms of graphs showing ILSS plotted against exposing time (days for hydrothermal and hygrothermal and in weeks for sea water) in figures: 4.6, 4.7, 4.8, 4.9, 4.10 and 4.11. The graphs include line as well as bar graphs.

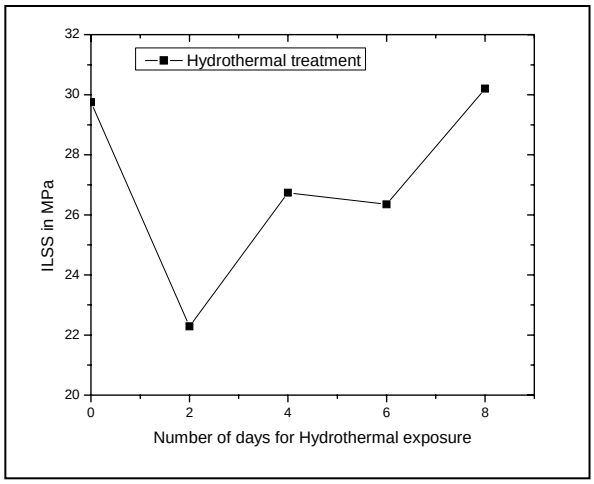

Fig: 4.6

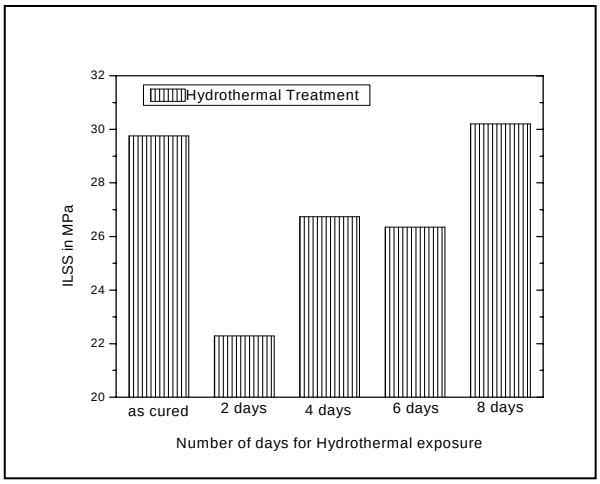

Fig: 4.7

(Variation of ILSS of hydrothermally treated sample with time without thermal shock)

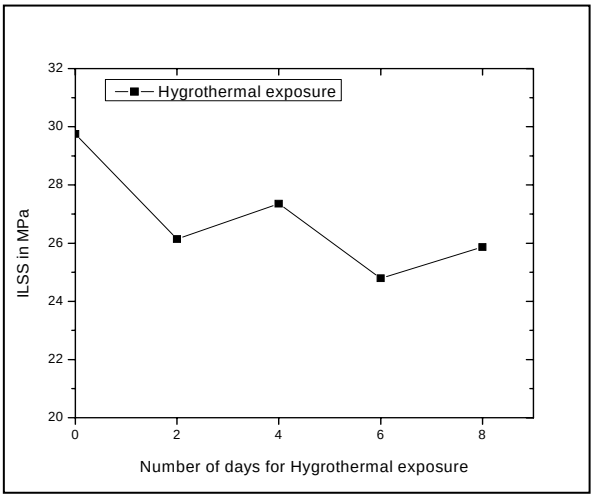

Fig: 4.8

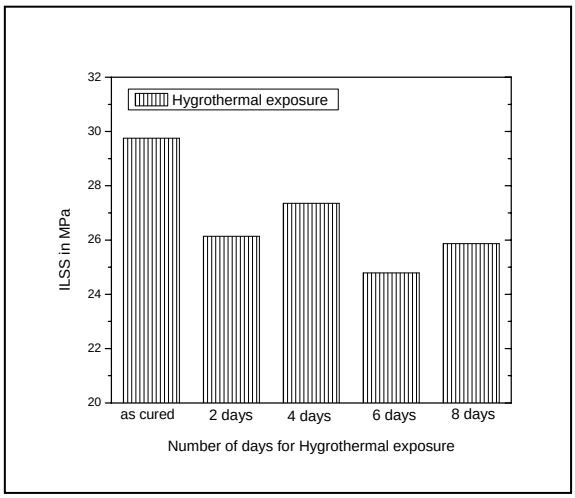

Fig: 4.9

(Variation of ILSS of hygrothermally treated sample with time without thermal shock)

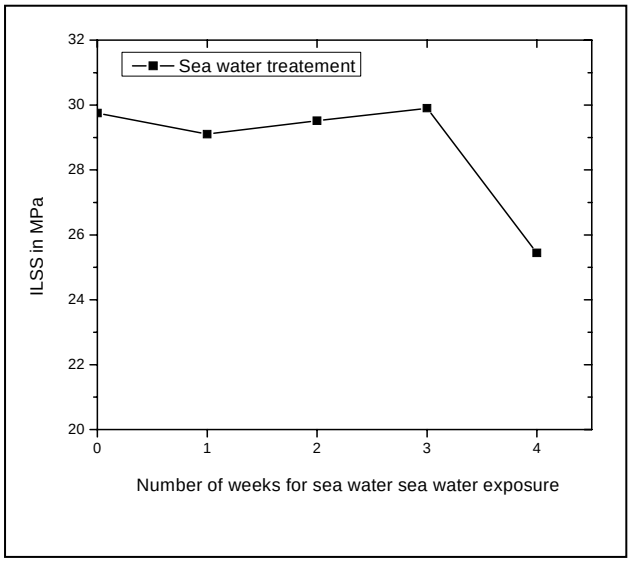

Fig: 4.10

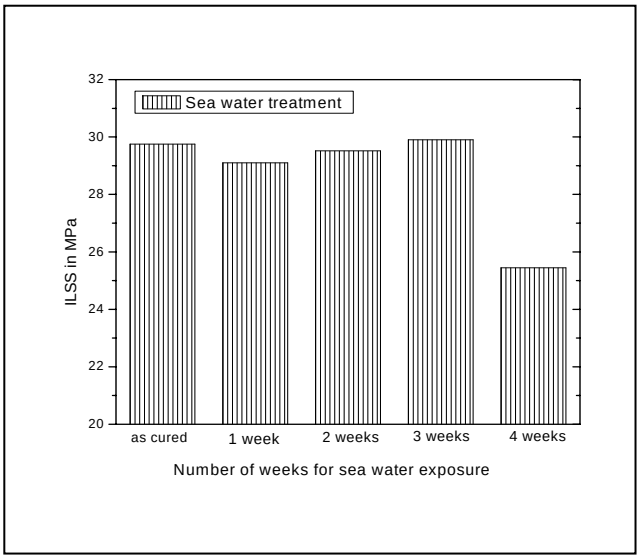

Fig: 4.11

(Variation of ILSS of sea water treated sample with time without thermal shock)

The data reveals the following:

(i) The ILSS of hydrothermally treated sample decreased for two days exposed sample from 'as cured' condition. From four to six days of exposure the ILSS approximately maintained the constant value and then increased.

(ii) The ILSS of hygrothermally treated sample gradually decreased from 'as cured' sample to eight days of exposing by maintaining the fluctuations within some range of values.

(iii) The ILSS of sea water treated sample decresed up to very small extent for initial moisture exposure. For first to third week the ILSS maintained approximately constant value, and then suddenly decreased up to very higher extent.

The results can be analyzed as below:

The reduction of ILSS of hydrothermally treated sample for initial moisture treatment may be related to the weakening effects of higher thermal and moisture induced swelling stresses at the interface and/or in the matrix resin [30]. It may also be hypothesized that this conditions environment could result in either breakdown of chemical bonds or secondary forces of attraction at interface. The ILSS further increased for consequent

moisture absorption due to the partial regeneration of bond strength is recovered for glass/epoxy composite. This increase may be related to the release of curing stress by the swelling stress.

The ILSS maintains approximately constancy from day four to six, pertaining the fact that, the composites attains the saturation of moisture content and then the further moisture absorption is blocked for certain period. Hence the reduction of ILSS is very less in this period.

The continuous reduction of ILSS for hygrothermally treated sample with fluctuation may be attributed due to generation of double hydrogen bond in the epoxy chain. Water at the interphase causes replacement of the covalent bonds between the siloxane backbone of the sizing material and the glass surface, with hydrogen bonds between the oxygen atoms on the fiber glass surface, water molecules at the interphase and the hydroxyl groups on the sizing material [48]. The absence of covalent bonds at the interphase leads to clear debonding of fibers from the matrix. As the result of which some adverse effects like debonding at fiber/matrix interfaces, microcracking in the matrix, fiber fragmentations, continuous cracks and reduction of ILSS occurred [23].

The formation of hydrogen bonds due to the availability of hydroxyl groups inside fiber/matrix interfaces causes the weakening of cross linking in epoxy chain. As the result of which, the cross linking density decreased. This leads to the generation of swelling stresses. The free volume inside the epoxy network increases. Hence the glass transition temperature reduced and relieves the internal stresses that were built up during the processing of the composite. This phenomenon called plasticization [24, 30] in turn may lower the modulus since the matrix become pliable. Due to the difference of coefficient of thermal expansion between fiber and polymer further develop residual stresses at the interfaces. These stresses along with the internal stresses relieved by plasticization weaken the brittle thermoset epoxy resin and/or the interfacial region of laminate.

The slight decrease of ILSS of sea water treatment for initial moisture exposure is due to the weakening of matrix due to formation of hydrogen bonds. The ILSS value approximately remains constant up to third week of exposure. This constancy can be revealed by the fact that the curing stress is nullified with that of the residual stress developed due to moisture absorption. The sudden decrease of ILSS values after third week may be explained as due to exchange of hydroxyl ion between the corresponding epoxy chains [46]. The segmentations of epoxy chain would have been occurred due to breaking of organic bonds present inside it. Correspondingly, a large amount of swelling stress generates which dominates the residual stress. Hence the interfacial delaminations occurred. This leads to the formation of cracks at the interface of glass/epoxy laminates.

4.3 INTER LAMINAR SHEAR STRENGTH WITH UP-THERMAL SHOCK

4.3.1 FOR HYDROTHERMALLY TREATED SAMPLE:

Table: 4.3 contains data relating inter laminar shear strength (ILSS) of hydrothermally treated sample after up-thermal shock treatment. The treatment was given by exposing the hydrothermally treated (2, 4, 6, 8 days) samples to -40^0C for durations (5, 10, 15, 20) minutes and immediately to $+50^0$C for 30 minutes. The detail of this treatment was discussed elsewhere (chapter-3, section-3.9.1). The ILSS of shocked sample was measured by INSTRON -1195 implementing the 3-point bend test method. The ILSS was measured with low cross head velocity i.e. 1mm/min.

TABLE: 4.3 (ILSS of hydrothermally treated sample after up-thermal shock treatment)

Hydrothermal Treatment 65^0C+dipped in distilled water In days	Up-Thermal Shock		Average Stress at Yield (MPa)	Average Load at Yield (KN)	Average ILSS in (MPa)
	-40^0C in minutes	$+50^0$C in minutes			
2	5	30	352.35	2.692	27.86584607
	10	30	361.35	2.811	28.58540864
	15	30	344.7	2.762	28.40979416
	20	30	353.7	2.44075	27.06277891
4	5	30	358.6	2.49725	27.91944868
	10	30	342.9	2.68325	27.38963519
	15	30	350.5	2.636	28.11883774
	20	30	349.9	2.77825	28.0484533
6	5	30	360.6	2.60375	27.1985777
	10	30	368.9	2.9335	29.5865774
	15	30	352.2	2.664	27.0163702
	20	30	339.75	2.60275	28.0547862
8	5	30	374	2.7525	29.4156445
	10	30	363.4	2.61225	27.9313296
	15	30	383.3	2.5815	26.8361526
	20	30	340.6	2.6065	26.893408

The data presented at Table: 4.3 was expressed in forms of graphs showing ILSS plotted against the time period of shock treatment (i.e. -40^0C for 5,10,15,20 minutes) in figure number-4.12 and 13. The line and the bar graph are shown in the same page.

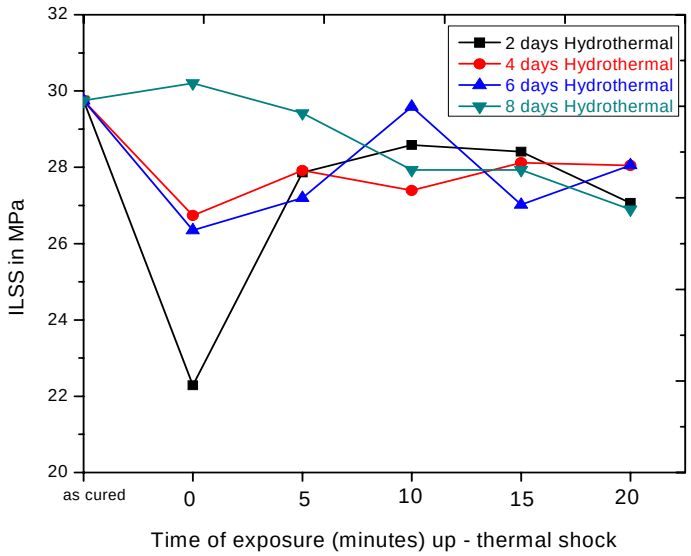

Fig: 4.12 (Variation of ILSS of hydrothermally treated sample with the time of exposure of up-thermal shock)

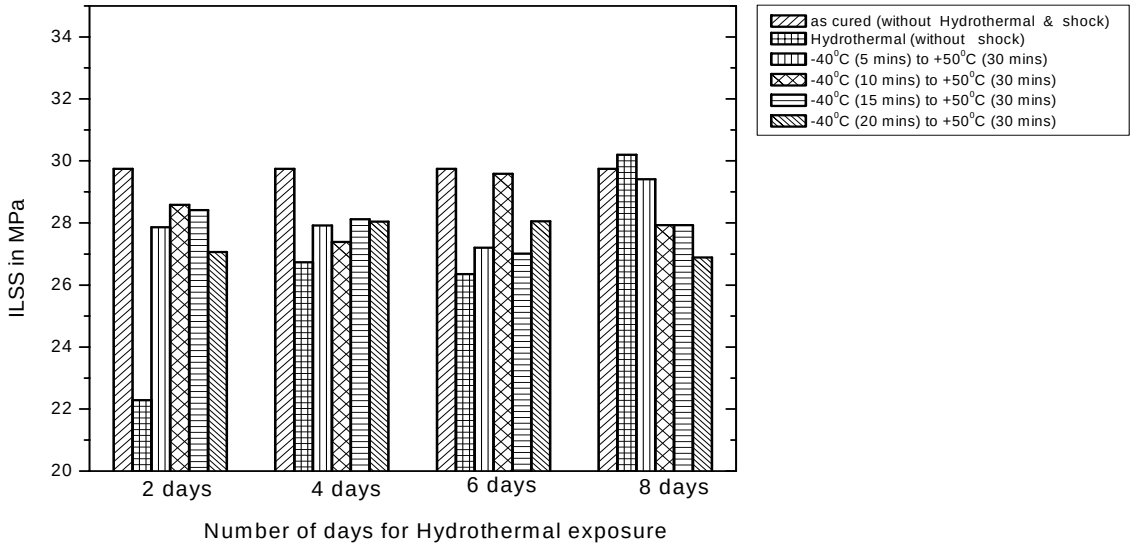

Fig: 4.13 (Variation of ILSS of hydrothermally treated sample with the time of exposure of up-thermal shock)

The data reveals the following

(i) The ILSS of up-thermally shocked hydrothermally treated sample for 2 days initially increased for shorter durations. With increase of shock time the ILSS decreased slowly up to very low extent.

(ii) The similar trend is observed for 4 days hydrothermally treated sample. But the initial increase of ILSS for shorter duration is less than that of 2 days hydrothermally treated sample. The ILSS maintained the value for longer duration of shock as obtained for shorter duration with some sorts of fluctuation within some range of values.

(iii) The 6 days hydrothermally treated sample showed increase in ILSS for the shock condition [-40^0C (5-10 minutes) to $+50^0$C (30 minutes)]. Then the ILSS decreased with a little increase for longer duration of shock.

(iv) The shocked hydrothermally treated sample for 8 days behaves in a different manner in comparison to others (2, 4, 6, days). The ILSS gradually decreased from shorter to longer duration of shock treatment.

(v) The ILSS of the entire shocked hydrothermally treated sample converged in between some range of values for longer duration of time.

The results can be analyzed as below:

The initial increment of ILSS for 2 days hydrothermally treated sample for shorter duration of shock may be attributed to the variation of rate of desorption of moisture (absorbed during the hydrothermal treatment) due to thermal contraction for -40^0C and expansion for $+50^0$C. The rate of moisture desorption is very less in sub ambient region where as the rate is very high in thermal region [47]. Hence maximum of the moisture content desorbed due to larger thermal gradient for shorter duration of shock. As the result of which the sample relaxed due to accommodation of the residual stress, generated due to post curing strengthening effect. This phenomenon might be responsible for the increase of interfacial adhesion strength [39].

The initial increase of ILSS for 4 and 6 days sample less than that of two days notwithstanding the fact that the rate of desorption remains same rather the amount of desorption is quite low compared to amount of moisture absorbed during hydrothermal treatment. Hence the stress relaxation is not so much prominent due to lower post curing strengthening than that of two days. The ILSS approximately maintains a constant value from shorter to longer duration of shock with some fluctuation within some range of values, which may be attributed to the continuing of stress relaxation up to the longer duration of shock. The rate of desorption of moisture during up-thermal shock may be comparable with that of moisture absorption during hydrothermal treatment for 4 days by which the ILSS increment is less in comparison to 2 days.

For the longer duration of shock the 6 days hydrothermally treated sample shows the decrease in ILSS. The residual stress generated due to differential thermal contraction and expansion may not able to accommodate, rather produce misfit of strain between the two components of composite. This misfit of strain may be due to additional interfacial cracking, which could have responsible for the interfacial degradation [39]. This could be related to quite large residual stress due to greater thermal expansion of the epoxy matrix. Higher thermal stresses might have started dominating over the cryogenic compressive stresses for a longer duration of up-thermal shock.

The decrement of ILSS for 8 days hydrothermally treated sample from shorter to longer duration may be analyzed due to absence of stress relaxation for this situation. The 8 days hydrothermally treated sample absorbed more moisture than that of 2, 4, 6 days of hydrothermal treatment. Here the amount of moisture desorption is very less as compared to amount of moisture absorbed by hydrothermal dipping. During up-thermal shock for different time periods the differential thermal contraction and expansion occurred. Hence the residual stress generated due to differential thermal contraction and expansion is much more than that of due to post curing effect for shorter to longer duration of shock. Hence the relaxation of interface between glass fiber and epoxy resin occurred due to differential contraction and expansion, which could have hampered due to no accommodation of stress. Hence the magnitude of stress relaxation is very less. This leads to the reduction of ILSS for shorter to longer duration of up-thermal shock.

The ILSS of the entire hydrothermally treated sample converged for longer duration of shock. This type of behavior may be attributed to the concept that at the longer duration of up-thermal shock the degradation of epoxy matrix and epoxy-glass interface/interphases is higher which dominates the duration of shock time for longer duration. The failure due to hydrothermal treatment for 6, 8 days due to swelling and plasticization may be comparable with that of failure due to up-thermal shock for longer duration for 2 and 4 days hydrothermally treated sample. Hence the converging nature of ILSS is noticeable for the longer duration of shock.

4.3.2 FOR HYGROTHERMALLY TREATED SAMPLE:

Table: 4.4 contains data pertaining inter laminar shear strength (ILSS) of hygrothermally treated sample after up-thermal shock treatment.

TABLE: 4.4 (ILSS of hygrothermally treated sample after up-thermal shock treatment)

Hygrothermal Treatment (60^0C+95% H.A. In days	Up-Thermal Shock		Average Stress at Yield (MPa)	Average Load at Yield (KN)	Average ILSS in (MPa)
	-40^0C in minutes	$+50^0$C in minutes			
2	5	30	381.1	2.74575	29.10919675
	10	30	373	2.51825	28.21134943
	15	30	331.4	2.39475	25.79976406
	20	30	363.8	2.4935	27.59160141
4	5	30	354.35	3.1725	32.30112383
	10	30	362.73	2.8716	32.9887671
	15	30	361.2	2.65225	28.24250581
	20	30	333.4	2.51075	26.16945733
6	5	30	324.9	2.36275	25.05218764
	10	30	338.975	2.575	26.36206763
	15	30	344.175	2.5155	26.39527128
	20	30	326.75	2.6875	26.93610685
8	5	30	333.875	2.43225	26.06924951
	10	30	324.73	2.532	26.27765041
	15	30	350.76	2.2816	26.15935552
	20	30	320.125	2.4575	25.50154275

The data presented at Table: 4.4 were expressed in terms of graphs showing ILSS plotted against the time period of the initial phase of the up-thermal shock treatment (i.e. -40^0C for 5,10,15,20 minutes) in figure: 4.14 and 4.15. In the final phase of up-thermal shock the time period of $+50^0$C was fixed i.e. 30 minutes. The line and the bar graph are shown in the same page.

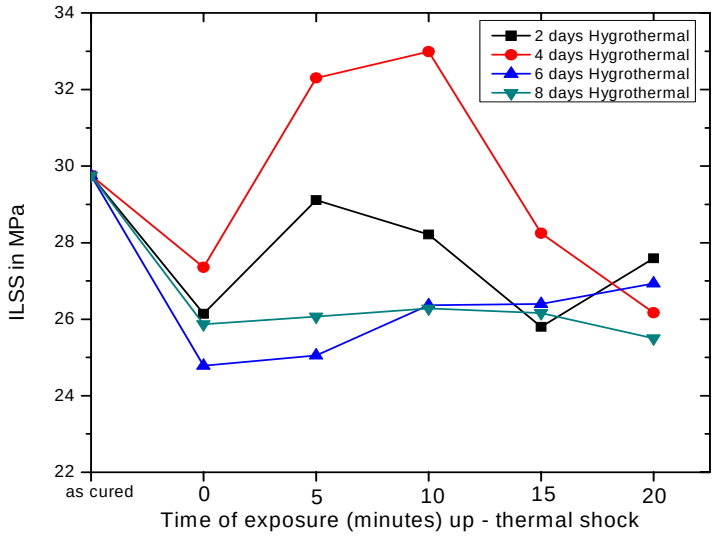

Fig: 4.14 (Variation of ILSS of hygrothermally treated sample with the time of exposure of up-thermal shock)

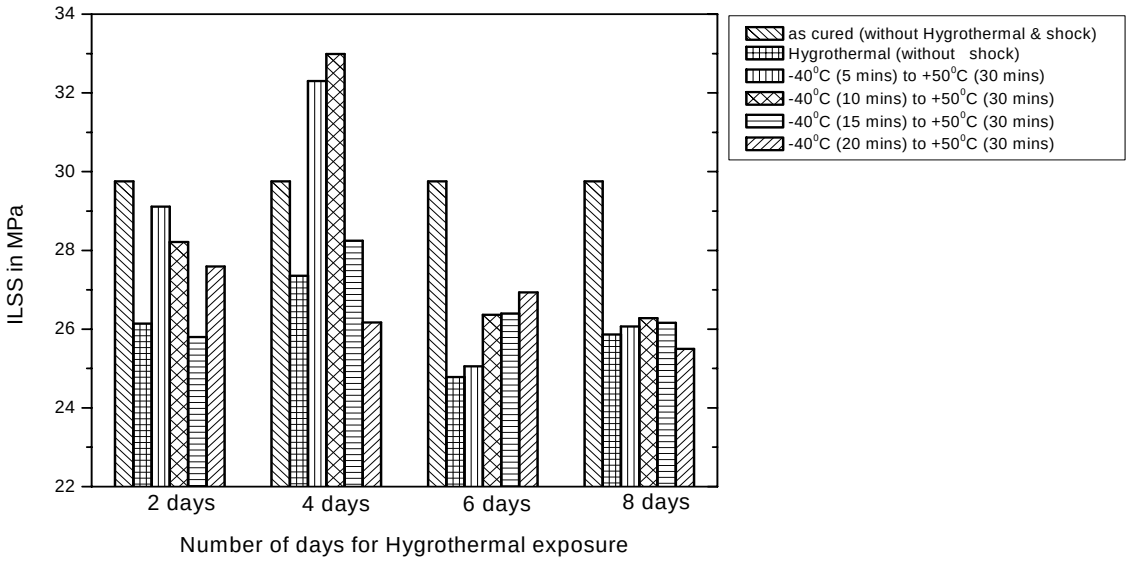

Fig: 4.15 (Variation of ILSS of hygrothermally treated sample with the time of exposure of up-thermal shock)

The data reveals the following:

(i) The 2 and 4 days hygrothermally treated sample showed a large variation of ILSS during the shock starting from shorter to longer duration. The ILSS increased up to some peak value for shorter duration of up thermal shock. The ILSS variation is much prominent in case of 4 days hygrothermally treated sample.

(ii) The ILSS decreased rapidly from a peak value up to a large extent for 2 and 4 days hygrothermally treated sample for longer exposing time of up-thermal shock. This decrement is higher in case of 4 days hygrothermally treated sample.

(iii) The ILSS increased for 6 days hygrothermally treated sample slowly up to very small extent from shorter to longer exposing time of up-thermal shock.

(iv) The ILSS maintained approximately one value from no shock condition to longer exposing time of up-thermal shock for 8 days hygrothermally treated sample.

(v) The ILSS value showed an increasing trend by exposing all the hygrothermally treated sample to up-thermal shock for shorter duration. For longer duration of shock, the ILSS decreased for all the samples.

The results can be analyzed as below:

Hygrothermally treated sample absorbed more moisture than that of hydrothermal and sea water treated sample as reported in section-4.1. When 2 and 4 days hygrothermally treated sample exposed to up-thermal shock treatment, the frozen moisture during the initial phase of the shock caused for the contraction in the composite structure. Hence the polymer-glass fiber interface enhances due to mechanical locking [39]. The moisture (absorbed during the hygrothermal treatment) desorbed more during the shorter duration of the shock [47]. Here the sample relaxed due to generation of residual stress, which might have accommodated in the interface of the composite. Hence ILSS increase for shorter duration

of up-thermal shock is observed here. The increase rate is higher for 4 days, as more moisture became frozen during the initial phase of the up-thermal shock.

For the longer duration of shock [-40^0C (15-20 minutes) to $+50^0$C (30 minutes)] the moisture desorption decreases. Here for longer duration of up-thermal shock, the thermal contraction due to -40^0C may be comparable with that of thermal expansion due to $+50^0$C. The generation of residual stress becomes less prominent. Hence the ILSS decreases by attaining a peak value.

As 6 days hygrothermally treated sample absorbed more moisture than that of 2 and 4 days (discussed earlier in chapter: 4, section-4.1), so more moisture become frozen in the initial phase of the thermal shock. Comparatively the moisture desorption occurred due to final phase of the up-thermal shock. Hence differential thermal contraction and expansion due to the two phase shock treatment is responsible for the maintaining of some thermal gradient from shorter to longer duration of shock. The corresponding moisture desorption for 6 days hygrothermally treated sample caused for the generation of residual stresses, which could have responsible for the increase of ILSS. The 6 days hygrothermally treated sample already reduced its strength from 'as cured' condition to hygrothermal condition by certain moisture degradative phenomena like plasticization and swelling [24], the increase of ILSS due to shock is less noticeable. For which the rate of increase of ILSS for 6 days is very low. Again in the 6 days hygrothermally treated sample the reduction of ILSS occurred due to absence of covalent bond at the interphase to occur debonding of fibers from the matrix. In the up-thermal shock treatment the generated residual stress is not so much sufficient to dominate the stress occurred due to swelling during hygrothermal treatment. For which the rate of increase of ILSS is less prominent in comparison to 2 and 4 days hygrothermally treated sample.

The ILSS value for 8 days hygrothermally treated sample maintained approximately constant value from shorter to longer duration of up thermal shock. This result can be analyzed as that of 6 days hygrothermally treated sample. The 8 days hygrothermally treated sample absorbed more moisture than that of other samples during hygrothermal treatment. The ILSS reduced from 'as cured' condition to hygrothermal treatment condition up to a large extent due to plasticization and swelling, as here the epoxy matrix become pliable.

With the application of up-thermal shock the variation of moisture desorption occurred due exposing from sub ambient region -40^{0}C to thermal region +50^{0}C. Here the strengthening effect by post curing due to moisture desorption is being nullified by the weakening effect caused due to some moisture degradation phenomena like plasticization and swelling.

In case of thermal shock after hygrothermal treatment the ILSS values show an increasing trend in all specimens due to mitigation of the thermal stress generated due to misfit of strains. But prolonged exposure for longer durations causes the mechanical property deterioration by reducing the ILSS due to formation of micro cracks and crazing. (More misfit stresses are generated due to differential coefficient of thermal expansion of the fiber and matrix) [47].

4.3.3 FOR SEA WATER TREATED SAMPLE:

Table: 4.5 contains the data relevant to the Inter laminar shear strength (ILSS) of sea water treated sample at room temperature after up-thermal shock treatment.

TABLE: 4.5 (ILSS of sea water treated sample after up-thermal shock treatment)

Sea Water Exposure (Room Temp.+ Dipped) In weeks	Up-Thermal Shock		Average Stress at Yield (MPa)	Average Load at Yield (KN)	Average ILSS in (MPa)
	-40^0C in minutes	$+50^0$C in minutes			
1	5	30	285.75	2.454	28.06282241
	10	30	276.775	2.8335	29.48954655
	15	30	275	2.6653	29.67941055
	20	30	272.025	2.82625	28.37947106
2	5	30	386.85	2.67925	29.88017445
	10	30	371.775	2.6955	28.95063848
	15	30	380.4	2.57275	29.07700732
	20	30	375.075	2.7335	29.30680037
3	5	30	354.5	2.754	29.01136172
	10	30	352.775	2.7385	28.51766837
	15	30	369.075	2.6625	28.52630023
	20	30	360.73	2.7926	28.52151866
4	5	30	392.866	2.7286	30.00764011
	10	30	361.2	2.76125	28.83704064
	15	30	360.5	2.77	29.26478573
	20	30	382.6	2.809	29.63504467

The data presented at Table: 4.5 was expressed in forms of graphs showing ILSS plotted against the time period of initial phase of up-thermal shock treatment (i.e. -40^0C for 5,10,15,20 minutes) in figure: 4.16 and 4.17. In the final phase of up-thermal shock the time duration of $+50^0$C was fixed i.e. 30 minutes. The line and the bar graph are shown in the same page.

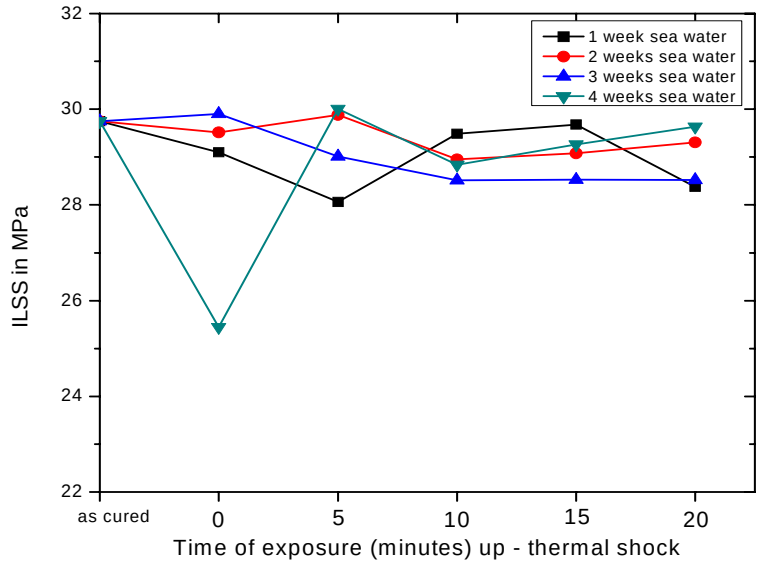

Fig: 4.16 (Variation of ILSS of sea water treated sample with the time of exposure of up-thermal shock)

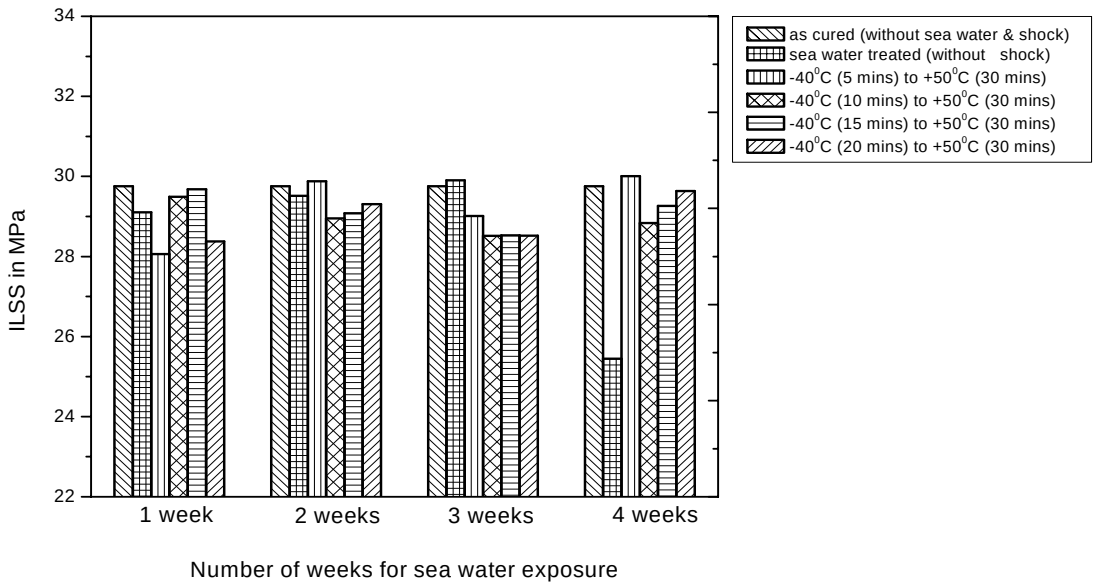

Fig: 4.17 (Variation of ILSS of sea water treated sample with the time of exposure of up-thermal shock)

The data reveals the following:

(i) The one week sea water treated sample shows the decrease in ILSS for initial duration of up-thermal shock. After that the ILSS increases slowly up to -40^{0}C for 15 minutes. Again the ILSS decrease occurs up to some extent for longer duration of shock the variation of ILSS is maintained within some limited value.

(ii) The 2 weeks sea water treated sample shows a slight increase in ILSS for shorter duration of up-thermal shock. After that, the sample shows approximately constant value for longer duration of shock.

(iii) The 3 weeks sea water treated sample shows the decrease in ILSS for initial period of shock, than remains unchanged for longer duration.

(iv) The ILSS increases for 4 weeks sea water treated sample for initial duration of shock. The variation of ILSS w.r.t. the time of duration of shock is very much negligible for longer duration of shock.

The results can be analyzed as below:

The initial decrement in ILSS value for 1 week and 3 weeks sea water treated sample can be related to the generation of lower degree of compressive stress during the sub ambient post curing time. The decrease in ILSS may be attributed to the debonding effect of up-thermal shock. The weakening effect due to shock may dominant over the post curing strengthening because of the availability of lesser conditioning time of up-thermal shock [39].

The ILSS again increases for 1 week sea water treated sample up to some peak value for further conditioning time of shock i.e. -40^{0}C (10 to 15 minutes) to +50^{0}C (30 minutes). This increase of ILSS may be attributed to further polymerization phenomena [39]. The cross linking confinement may be limited to very large region of matrix space available so that free volume will decrease. The packing density of the polymeric network inside the polymer increases. This gives rise to the further increase of ILSS up to some extent.

The ILSS will be decreased for 1 week sea water treated sample for longer conditioning time of shock i.e. -40^0C (15 to 20 minutes) to $+50^0$C (30 minutes). This may be related to the availability of more exposing time of shock by which the amount of sea water absorbed during immersed condition gets desorbed. The bulky nature of sea water desorbed during the shock by which the porosity level of interface increases up to some extent. For which the ILSS decreased as shown in fig: 4.16. But this decrease is not so much prominent as the moisture peak up level is low in comparison to other exposing environment of moisture i.e. hydrothermal and hygrothermal exposure.

The slight increase of ILSS for 2 weeks sea water treated sample for lesser conditioning time of shock may be attributed to the swelling due to relieve of residual stress, which built up during the fabrication of the composite. The ILSS further decreased due to misfit of strain occurred during the moisture absorption. This may be due to the generation of localized stresses, which are responsible for the nucleation of crack and further growth due to propagation of crack in the matrix and matrix-fiber interface. This will give rise to the reduction of ILSS as shown in fig: 4.16. But the reduction rate of ILSS is not so much prominent for 2 weeks sea water treated sample, as due to low desorption rate of moisture. Here the curve maintains approximately straight line for longer conditioning time of shock.

The ILSS value decreased from ‘as cured’ condition to longer duration of up-thermal shock for 3 weeks sea water treated sample. This result may be analyzed due to degradation phenomena by sea water immersion as well as due to up-thermal shock. Though sea water treated sample absorbed less moisture in comparison to hydrothermal and hygrothermal treatment, but the time of exposing to sea water is maximum. The sample came more in contact with sea water in immersed condition. As the result of which the hydroxyl ion exchange occurred between corresponding epoxy chains [46].Hence the breaking of organic bonds was taken place due to segmentation of epoxy chains. Again due to up-thermal shock, residual stress generated due to varying moisture desorption in -40^0C and in $+50^0$C. Whatever the ILSS increase may suspect due to the residual stress generation that is dominated by some failure (cracks, delaminations, debonding) arise during sea water immersion. For shorter to longer duration of up-thermal shock, the ILSS slowly decreased

for 3 week sea water treated sample. the weakening effect due to sea water immersion may nullified due to post curing strengthening because of thermal shock for longer duration. The ILSS remains unchanged for 3 weeks sea water treated sample for longer duration of up-thermal shock.

The ILSS value is observed to be increasing for 4 weeks sea water treated sample for shorter duration of shock i.e. -40^0C (0 to 5 minutes) to $+50^0$C (30 minutes). This may be attributed to the post curing strengthening due to generation of residual stress during moisture desorption in up-thermal shock treatment. Again, the 4 weeks sea water treated sample absorbed more sea water than that of 1 week, 2 weeks and 3 weeks sea water treated sample. Hence during initial phase of up-thermal shock the mechanical locking occurs between fibers-polymer interfaces due to low temperature exposure (-40^0C). The poly silaxane layer is more expanded so that the epoxy polymer experienced more area of fiber via silaxane layer. Hence the interfacial adhesion increases up to certain extent [48]. For further duration of the shock, the moisture desorption decreases to lower the generation of residual stress. Whatever stress generated during shorter duration that may not be accommodate during longer duration of the shock. As the result of which, the ILSS decreases for longer duration of up-thermal shock.

4.4 INTER LAMINAR SHEAR STRENGTH WITH DOWN-THERMAL SHOCK

4.4.1 FOR HYDROTHERMALLY TREATED SAMPLE:

Table: 4.6 contains data pertaining inter laminar shear strength (ILSS) of hydrothermally treated sample after down-thermal shock treatment. The treatment was given by exposing the hydrothermally treated (2, 4, 6, 8 days) samples to $+50^0$C for durations (5, 10, 15, 20 minutes) and immediately to -40^0C for 30 minutes. The detail of this treatment was discussed elsewhere (Chapter -3, section-3.9.2). The ILSS of shocked sample was measured by INSTRON-1195 implementing the 3-point bend test method. The ILSS measured with low loading speed i.e. 1mm/min.

TABLE: 4.6 (ILSS of hydrothermally treated sample after down-thermal shock treatment)

Hydrothermal Treatment 65^0C+dipped in distilled water In days	Down-Thermal Shock		Average Stress at Yield (MPa)	Average Load at Yield (KN)	Average ILSS in (MPa)
	$+50^0$C in minutes	-40^0C in minutes			
2	5	30	322.83	2.422	27.35490147
	10	30	352.033	2.3356	26.86627356
	15	30	369.16	2.6496	29.083343819
	20	30	343.65	2.51425	27.18016707
4	5	30	364.1	2.56525	27.83342118
	10	30	371.8	2.57225	28.00394346
	15	30	356.025	2.49275	27.0278754
	20	30	359	2.572	27.53501866
6	5	30	346.45	2.5025	26.957945
	10	30	342.7	2.463	26.3127496
	15	30	374.475	2.53475	26.9043316
	20	30	340.525	2.4362	25.9768443
8	5	30	329.375	2.56625	26.99973267
	10	30	380.2	3.022	30.56411021
	15	30	352.6	2.65875	27.53844188
	20	30	356.3	2.64775	27.980693

The data presented at Table: 4.6 was expressed in terms of graphs showing ILSS plotted against the time period of the shock treatment (i.e. $+50^0$C for 5,10,15,20 minutes) in figure: 4.18 and 4.19. The line and the bar graph are shown in the same page.

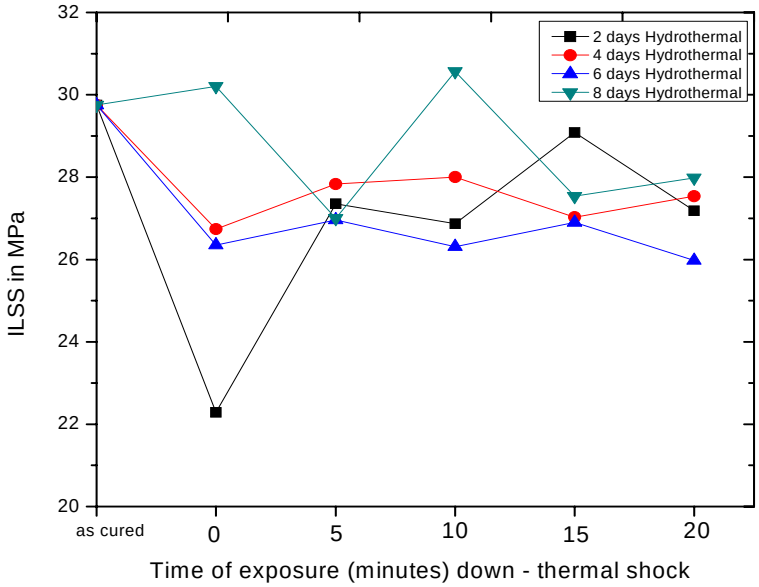

Fig: 4.18 (Variation of ILSS of hydrothermally treated sample with the time of exposure of down-thermal shock)

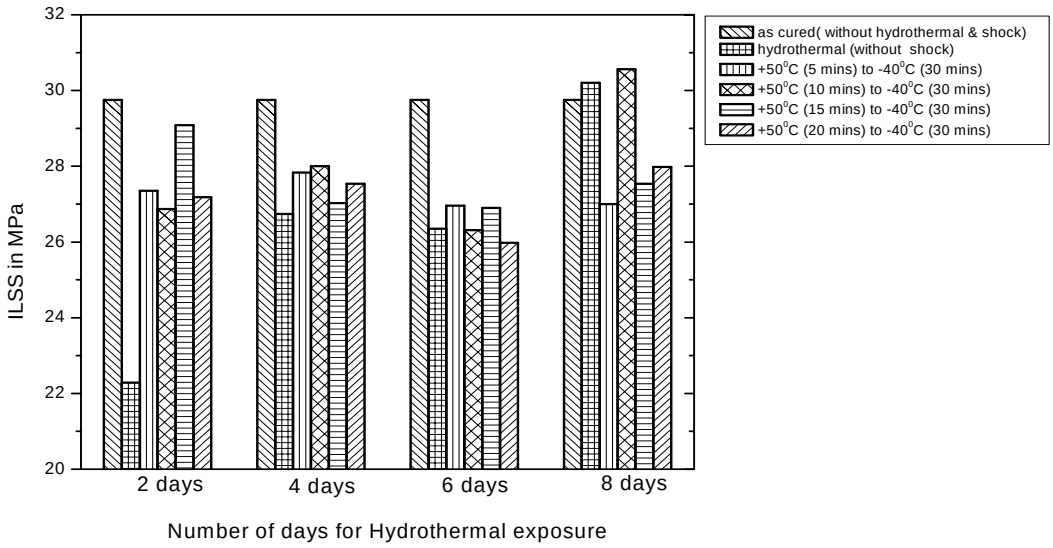

Fig: 4.19 (Variation of ILSS of hydrothermally treated sample with the time of exposure of down-thermal shock)

The data reveals the following:

(i) The 2 days hydrothermally treated sample shows an increase in ILSS starting from shorter to longer duration of down-thermal shock with some fluctuations. The increase in ILSS is more prominent for shorter duration.

(ii) The four days hydrothermally treated sample also shows increase in ILSS for shorter duration of shock. The ILSS further maintains a fluctuation/variation within a limited value for longer duration of shock. Here the ILSS increase is less prominent than that of 2 days hydrothermally treated sample.

(iii) A fluctuation of ILSS within some range of values is observed for 6 days hydrothermally treated sample for shorter to longer duration of down-thermal shock.

(iv) An unusual in ILSS is observed for 8 days hydrothermally treated sample after down-thermal shock. Large variation in ILSS is observed within some range of values from shorter to longer duration of shock. For the duration $+50^0$C (5 to 10 minutes) to -40^0C (30 minutes) the ILSS increase more than that from as cured sample.

(v) ILSS of the entire hydrothermally treated sample converge within some range of values for longer duration of down-thermal shock.

The results can be analyzed as below:

The increase of ILSS for 2 days hydrothermally treated sample for shorter to longer duration of down thermal shock may be attributed to the cryogenic hardening of the matrix phase at low temperatures [14]. Moisture desorption occurs in the initial phase of down thermal shock i.e. $+50^0$C (5 to 20 minutes). In the final phase of the shock (-40^0C) the remained moisture inside the specimen after moisture desorption gets frozen, which might have responsible of providing mechanical keying between fiber and polymer interface [39]. As 2 days hydrothermally treated sample absorbed very little moisture, the frozen moisture during final phase of the down-thermal shock creates very small residual stress due to contraction, which may not exceed the shear strength of epoxy resin with loading of

crosshead of INSTRON. As the result of which, the increase of ILSS is observed during down-thermal shock starting from shorter to longer duration of shock.

For the shorter duration of shock the ILSS increases up to some extent for 4 days hydrothermally treated sample. This result may be attributed to the generation of residual stresses, which built up due to thermal contraction between fiber and matrix during sub ambient cooling (-40^0C). During sudden cooling from $+50^0$C to -40^0C, the residual stresses may responsible for the enhancement of fiber-polymer interfacial adhesion by mechanical locking [39]. In this duration the polymer may entrap more between corresponding fibers. This might have lead to the increase of ILSS up to some extent. Here the ILSS increase is less prominent than that of 2 days hydrothermally treated sample due to presence of moisture in 4 days sample. The variation of ILSS for 4 days hydrothermally treated sample may be due to variation of duration of down-thermal shock in first phase. This may affect the generation of residual stresses leading to either deterioration or enhancement of mechanical properties [14].

The initial rise of ILSS in 6 days hydrothermally treated sample for shorter duration of shock may be attributed to the formation of strong double hydrogen bond in the epoxy matrix or at the interface [37]. Moisture desorption during initial phase of down-thermal shock may be the driving force for this phenomenon. A fluctuation in ILSS within some range of values for this sample is observed from shorter to longer duration of shock. During final phase of the down-thermal shock (-40^0C), high residual stresses can build up within the fibrous composite materials due to different coefficients of thermal expansion of fiber and the epoxy matrix. The polymer matrix experiences embrittlement which can also affect the properties of the composite [39]. When the sample arrives at the sub ambient region from thermal instantly, it might have affected generation of residual stresses leading to either deterioration or enhancement of mechanical properties [14]. The increase or decrease of ILSS for certain timing of the shock remains uncertain.

Same observation for 8 days hydrothermally treated sample can be explained as that of 6 days sample. But the ILSS increase for the period $+50^0$C (5 to 10 minutes) to -40^0C (30 minutes) is more prominent. This may be attributed to the polymerization of the remaining unopened epoxide molecules by additional ring opening polymerization mechanism during

adsorption of moisture by the application of down-thermal shock [37]. The moisture adsorbed during initial phase of down-thermal shock may induce the additional ring opening polymerization. This phenomenon is responsible for increase of amount of cross-linking at the interphase region which helps in completion of the left curing. Again, during final phase of down-thermal shock (-40^0C), the remained moisture gets frozen which may be responsible for the enhancement of interfacial adhesion by mechanical keying [39]. The increase of ILSS during this particular period of down-thermal shock is more noticeable than that of 6 days as due to less absorption of moisture in case of later one.

The ILSS of the entire hydrothermally treated sample converged for longer duration of shock. This type of behavior may be attributed to the concept that at the longer duration of down-thermal shock the degradation of epoxy matrix and epoxy-glass interface/interphases is higher which dominates the duration of shock time for longer duration. The failure due to hydrothermal treatment for 6, 8 days due to swelling and plasticization may be comparable with that of failure due to down-thermal shock for longer duration for 2 and 4 days hydrothermally treated sample. Hence the converging nature of ILSS is noticeable for the longer duration of shock.

4.4.2 FOR HYGROTHERMALLY TREATED SAMPLE:

Table: 4.7 contain data pertaining inter laminar shear strength (ILSS) of hygrothermally treated sample after down-thermal shock treatment.

TABLE: 4.7 (ILSS of hygrothermally treated sample after down-thermal shock treatment)

Hygrothermal Treatment 60^0C+95% H.A. In days	Down-Thermal Shock		Average Stress at Yield (MPa)	Average Load at Yield (KN)	Average ILSS in (MPa)
	+50^0C in minutes	-40^0C in minutes			
2	5	30	349.2	2.5555	27.22543107
	10	30	354.2	2.6705	28.11681961
	15	30	313.8	2.4335	25.39177902
	20	30	344	2.4875	26.39834237
4	5	30	340.5	2.512	26.86274022
	10	30	331.2	2.39875	25.91593275
	15	30	345.6	2.57975	27.30502614
	20	30	333.9	2.76875	27.09992099
6	5	30	330.875	2.27425	24.88336309
	10	30	339.275	2.44375	26.24623779
	15	30	327.225	2.38725	25.13073578
	20	30	304.475	2.511	25.166677
8	5	30	316.45	2.67825	26.2002311
	10	30	343.675	2.66575	27.2611764
	15	30	318.75	2.0655	21.7926418
	20	30	318.65	2.473	25.3528551

The data presented at Table: 4.7 was expressed in terms of graphs showing ILSS plotted against the time period of down-thermal shock treatment (i.e. +50^0C for 5,10,15,20 minutes) in figure: 4.20 and 4.21. The line and the bar graph are shown in the same page.

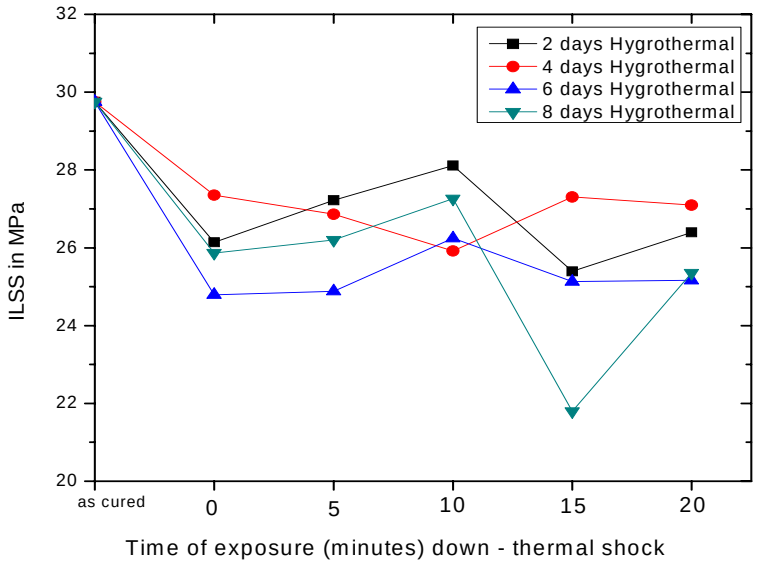

Fig: 4.20 (Variation of ILSS of hygrothermally treated sample with the time of exposure of down-thermal shock)

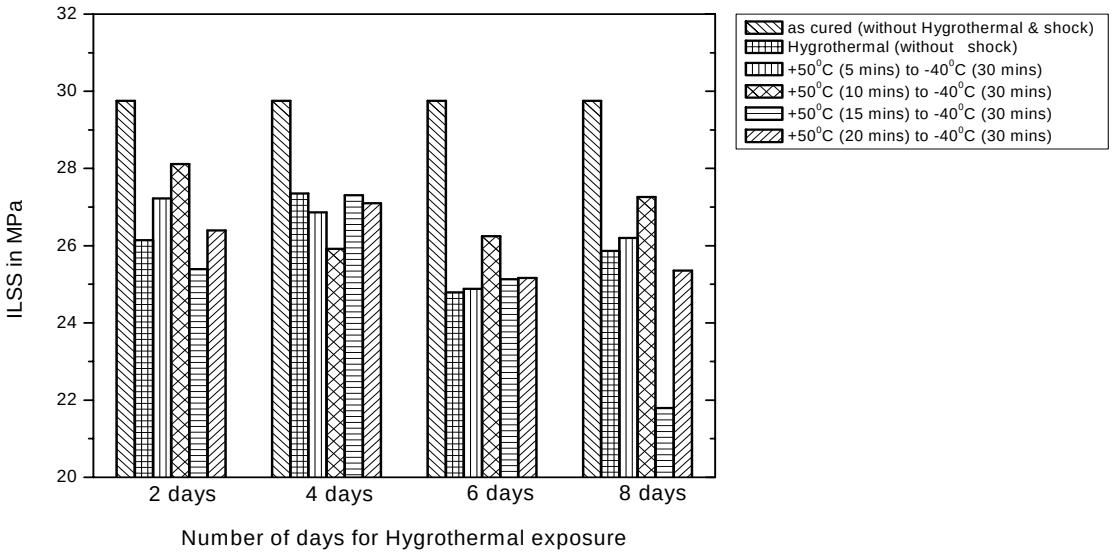

Fig: 4.21 (Variation of ILSS of hygrothermally treated sample with the time of exposure of down-thermal shock)

The data reveals the following:

(i) The 2, 6 and 8 days hygrothermally treated samples show the response towards the down-thermal shock in a similar manner. The ILSS for these samples increases for shorter duration of shock i.e. for $+50^0$C (0 to 10 minutes) to -40^0C (30 minutes). The decrease in ILSS from a peak value is observed for longer duration of shock. This fall of ILSS is more prominent in case of 8 days hygrothermally treated sample.

(ii) The 8 days hygrothermally treated sample shows the increase in ILSS for longest duration of shock i.e. $+50^0$C (15 to 20 minutes) to -40^0C (30 minutes).

(iii) The 4 days hygrothermally treated sample behaves in a different manner than that of other sample. The ILSS first decreases for shorter duration of shock and then increase for longer duration.

(iv) The ILSS of 6 and 8 days hygrothermally treated sample at longest duration of shock converge within a single value. The similar trend is valid for 2 and 4 days sample but the convergence lies within a range of value of ILSS.

The results can be analyzed as below:

The increase in ILSS for 2, 6 and 8 days hygrothermally treated sample for the shorter duration of shock may be attributed to the enhancement of interfacial adhesion by mechanical locking due to frozen moisture during the second phase of the down-thermal shock i.e. -40^0C. During first phase of this shock ($+50^0$C) for shorter duration, the moisture (absorbed during hygrothermal treatment) desorbed, which might have responsible for the leave of porosity inside the sample. This porosity level depends upon the extent of moisture absorbed during hygrothermal treatment for different time periods. Again in the second phase of the down-thermal shock the frozen moisture due to -40^0C reduces the void by contraction. This may helps further development of mechanical locking at the fiber/matrix interface. The induced mechanical keying factor due to differential contraction might have dominated over the weakening effect of thermal shock for shorter conditioning time. The

cryogenic conditioning causes the differential contraction and may increase the resistance to debonding by better adhesion at the interface [14, 60].

The decrease in ILSS for 2, 6 and 8 days hygrothermally treated sample for longer duration of shock may be attributed to the weakening effect due to down-thermal shock. For the longer conditioning time of down-thermal shock; the rate of desorption of moisture due to $+50^0$C may be comparable with the rate of freezing of moisture due to -40^0C. Here the mechanical keying due to frozen moisture might have dominated by the large misfit of strain at the interface due to longer conditioning of shock. The differences in thermal expansion coefficient of the fiber and epoxy matrix may result in the development of misfit of strain at the fiber/matrix interface [60]. There may be loosening of contact between matrix and fiber due to longer conditioning time for which the ILSS decrease is observed for this situation. But this fall in ILSS is more prominent for 8 days hygrothermally treated sample. This result may be related to the incompletion of the interfacial relaxation due to no accommodation of higher degree of cryogenic compressive stresses, which generated due to greater extent of frozen moisture during the second phase of the down-thermal shock. This is happened due to absorption of more moisture in case of 8 days hygrothermally treated sample. Here the availability of post curing time might have dominated by the generation of cryogenic compressive stresses.

The further increase of ILSS for 8 days hygrothermally treated sample for maximum duration of down-thermal shock may be attributed to the cryogenic hardening of the matrix phase at low temperature. The polymer chain gets frozen during the final phase of shock, which is more prominent in case of 8 days hygrothermally treated sample. For the maximum duration of shock; the deformation process might have reduced, resulting in less polymer relaxation i.e. it gets hardened. Residual stresses build up due to differential thermal contraction between fiber and matrix during sudden cooling from thermal region ($+50^0$C), which may be responsible for the increase of interfacial adhesion [14].

The initial decrement of ILSS for lesser conditioning time of down-thermal shock for 4 days hygrothermally treated sample may be analyzed due to high residual stresses which can build up within the fibrous composite material due to different coefficients of thermal expansion at the fiber and the matrix. These high residual stresses may not accommodate in

the interface of the composite. At low temperature the polymer matrix experiences embrittlement which might be responsible for the decrease of ILSS. The combined elevated and cryogenic temperature thermal shock may produce substantially greater amount of damage in 4 days hygrothermally treated sample and this damage may accelerate the failure effect produced during hygrothermal moisture treatment [14].

The further increase of ILSS for this sample (4 days) for higher conditioning time of down-thermal shock may be attributed to release of post curing shrinkage stresses by the hygroscopic swelling stress developed during hygrothermal moisture absorption [37]. Again the interfacial adhesion increase may be due to further polymerization phenomenon which might be responsible for the increment of cross-linking density at longer conditioning time of down-thermal shock [39].

4.4.3 FOR SEA WATER TREATED SAMPLE:

Table: 4.8 contains data pertaining inter laminar shear strength (ILSS) of sea water treated sample after down-thermal shock treatment.

TABLE: 4.8 (ILSS of sea water treated sample after down-thermal shock treatment)

Sea Water Exposure (Room Temp.+ Dipped) In weeks	Down -Thermal Shock		Average Stress at Yield (MPa)	Average Load at Yield (KN)	Average ILSS in (MPa)
	$+50^0$C in minutes	-40^0C in minutes			
1	5	30	280.866	2.651	28.3836653
	10	30	279.733	2.7843	29.60705023
	15	30	280.05	2.811	29.65170761
	20	30	266.066	3.116	30.95091924
2	5	30	365.775	2.602	28.24201892
	10	30	355.675	2.87975	28.95367519
	15	30	372.25	2.7805	29.12048929
	20	30	358.75	2.768	28.88189313
3	5	30	365.8	2.743	28.86340909
	10	30	362.4	2.83425	28.67770848
	15	30	362.8	2.7835	28.84331559
	20	30	359.3	2.95775	29.80962734
4	5	30	369.75	2.88375	29.57134812
	10	30	352.475	2.7205	28.15005103
	15	30	349.325	2.6405	28.04930073
	20	30	309.2	2.227	24.23586506

The data presented at Table: 4.8 was expressed in terms of graphs showing ILSS plotted against the time period of shock treatment (i.e. $+50^0$C for 5,10,15,20 minutes) in figure: 4.22 and 4.23. The line and the bar graph are shown in the same page.

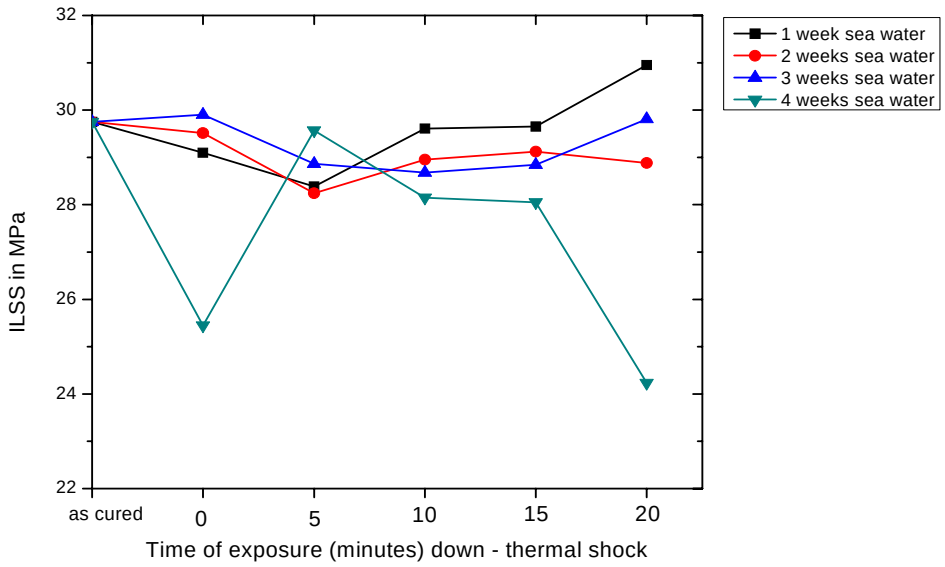

Fig: 4.22 (Variation of ILSS of Sea Water treated sample with the time of exposure of down – thermal shock)

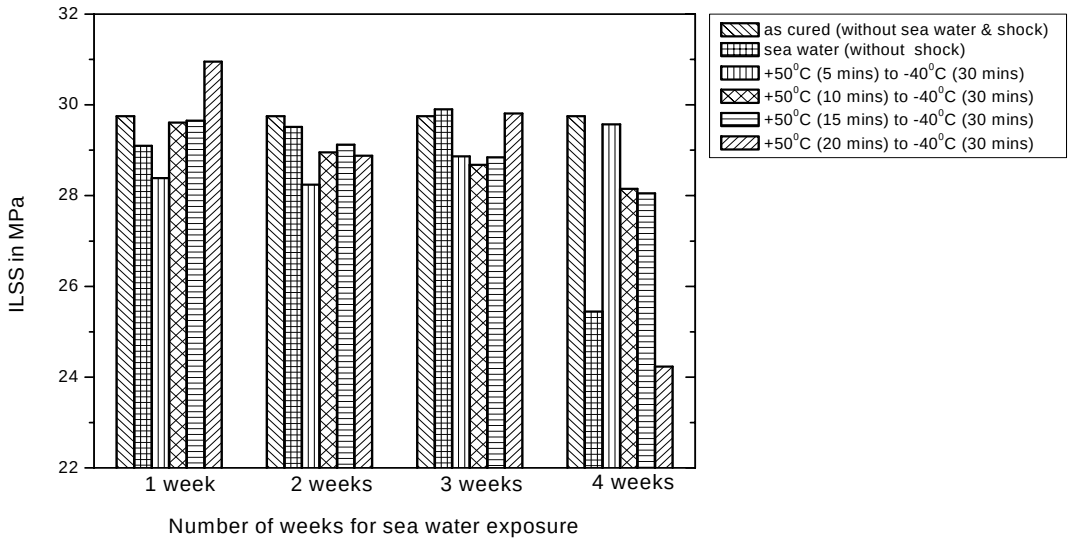

Fig: 4.23 (Variation of ILSS of Sea Water treated sample with the time of exposure of down-thermal shock)

The data reveals the following:

(i) The 1 week, 2 weeks and 3 weeks sea water treated samples show the similar trend in ILSS after down-thermal shock. The ILSS first decrease slightly for shorter duration of shock and then increase for longer duration.

(ii) The initial increment of ILSS for shorter duration is more prominent in case of 1 week sea water treated sample and less in case of 2 weeks sea water treated sample. For the longest duration of down-thermal shock the ILSS of 2 weeks sea water treated sample decreased up to very low extent.

(iii) The 4 weeks sea water treated sample behaves in a different manner compared to other samples. The ILSS first increases for short duration of the shock i.e. $+50^0$C (0 to 5 minutes) to -40^0C (30 minutes). After attaining a peak value the ILSS decrease occurs for further conditioning time of shock. For maximum duration of the shock; the ILSS falls rapidly up to very low extent for this sample.

The results can be analyzed as below:

The initial decrement of ILSS for 1 week, 2 weeks and 3 weeks sea water treated sample may be attributed to the damaging effect due to down-thermal shock. Here the moisture inside the sample is not in distilled state rather in saline. During desorption of moisture, the bulky nature of salt water may exhibit some localized stress upon the interface [56]. Again during final phase of down-thermal shock the freezing of moisture remains incomplete due to presence of salts. During loading of crosshead, the mobilized salt ions may react with the epoxy chain to create chemical degradation. This might have caused for the initial decrease of ILSS for the samples mentioned above.

For further conditioning time of down-thermal shock the ILSS increases for 1 week, 2 weeks and 3 weeks sea water samples. This may be analyzed by partial regeneration of bond strength between fiber/matrix interfaces via poly silaxane layer. For higher duration of shock; the sample comes in intact with $+50^0$C for larger intervals. Hence the moisture (absorbed during sea water exposing) desorbs more for this condition. For which, the glass fiber experiences the further moist environment by which the sized glass fiber may degrade

chemically. But this moist environment can create a region where larger surfaces of fiber and matrix participate in the adhesion process. This larger contact area/region allows the load to transfer to the fiber more effectively thus maintaining the better interfacial adhesion [48]. This increase of ILSS for 1 week sea water treated sample is more. This may be due to enhancement of this process for this sample than that of others. The 2 and 3 weeks sea water treated sample may promote the plasticizing effect of the moisture desorption of sea water for initial duration of down-thermal shock. So ILSS decrease for this case is less as compared to 1 week sea water treated sample.

The initial increment of ILSS for 4 weeks sea water treated sample for shorter duration of down-thermal shock may be attributed to the development of mechanical locking at the fiber/matrix interface [60]. The mechanical keying factor might be dominating over the weakening effect of down-thermal shock for short conditioning time. Again the -40^0C conditioning caused the differential contraction and might have increased the resistance to debonding by better adhesion at the interface.

The decrement of ILSS for this sample for further conditioning time of shock may be related to the large misfit strain at the interface. This is happened due to differences in the thermal expansion coefficients of the fiber and matrix. For the maximum duration of the shock; the rapid fall of ILSS from a peak value may be attributed to the formation of matrix and interfacial crackings [60]. Again in this situation, the higher percentage of moisture desorption may promote the crack initiation and further growth of it. These cracks may have been propagated to the interface of the composite.

4.5 EFFECT OF UP-THERMAL SHOCK & DOWN-THERMAL SHOCK ON GLASS TRANSITION TEMPERATURE (T_g)

The variations of T_g (Glass Transition Temperature) as consequence to exposure to different environments followed by up-thermal shock and down-thermal shock are presented in table: 4.9. The table also houses the same data for different environments without any thermal shock for the purpose of a comparison. Samples with extreme conditions of exposure and thermal shock treatment are chosen, on the basis of time of exposure of thermal treatment for a comparative study. The T_g data, on the basis of above, for hydrothermal and hygrothermal exposure for 8 days and sea water exposure for 4 weeks with up-thermal and down-thermal shocks as well as no thermal shock are presented only. The onset and midpoint value of T_g are separately mentioned. The scanning was done over a temperature of 30^0C to 150^0C with a scan rate 10^0C/min temperature variation. The DSC measurements were performed on Mettler-Toledo 821 software with Alternating DSC (ADSC) module. The details of the procedure adopted has been discussed elsewhere, (Chapter-3, section-3.10.1) in the thesis.

TABLE: 4.9 Variation of Glass Transition Temperature (T_g)

Moisture Shock Treatment / Treatment	**Glass Transition Temperature (degree centigrade)**					
	Hydrothermal Treatment **(8 DAYS)**		Hygrothermal Treatment **(8 DAYS)**		Sea Water Treatment **(4 WEEKS)**	
	Onset	Mid point	Onset	Mid point	Onset	Mid point
No Shock Treatment	89.90	99.75	96.13	107.45	75.76	83.82
Up – thermal shock **-40^{0}C (20 minutes) to +50^{0}C (30 minutes)**	88.37	98.52	56.75	62.03	72.72	81.70
Down – Thermal shock **+50^{0}C (20 minutes) to -40^{0}C (30 minutes)**	89.57	102.41	94.21	106.71	74.59	82.82

The T_g variation data is plotted in fig: 4.24 in the shape of a graph and in fig: 4.25 in the shape of a bar diagram.

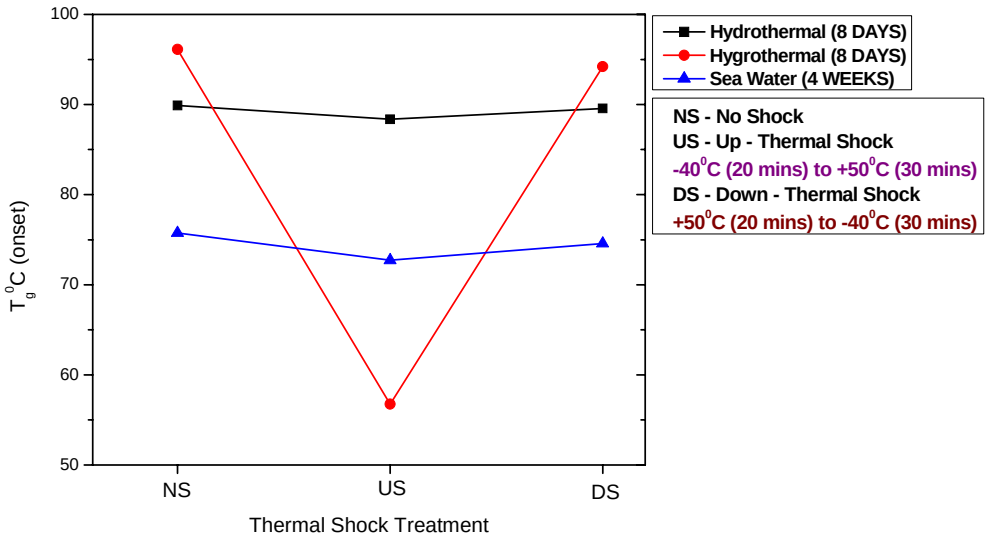

Fig: 4.24 (Variation of Glass transition temperature of different moisture treated sample w.r.t. different thermal shock treatment)

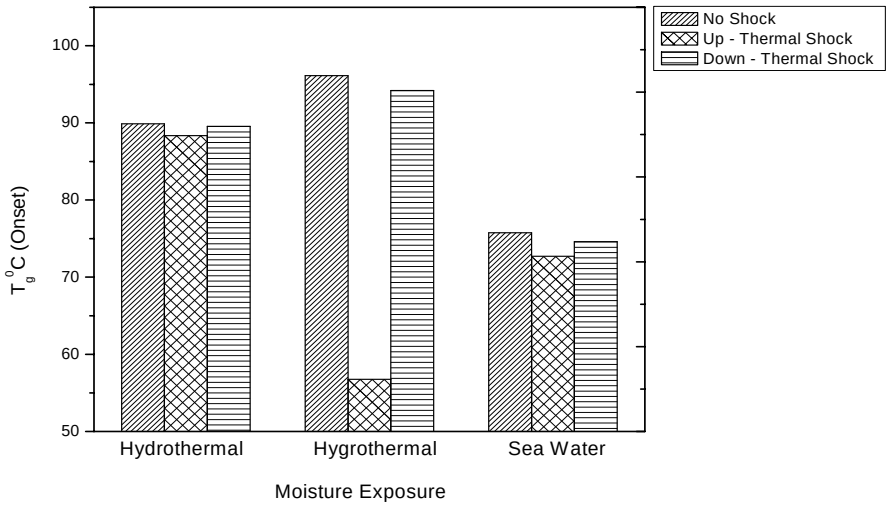

Fig: 4.25 (Variation of Glass transition temperature of different moisture treated sample w.r.t. different thermal shock treatment)

The actual T_g variation curves as obtained from the test module are presented in fig: 4.26 through fig: 35.

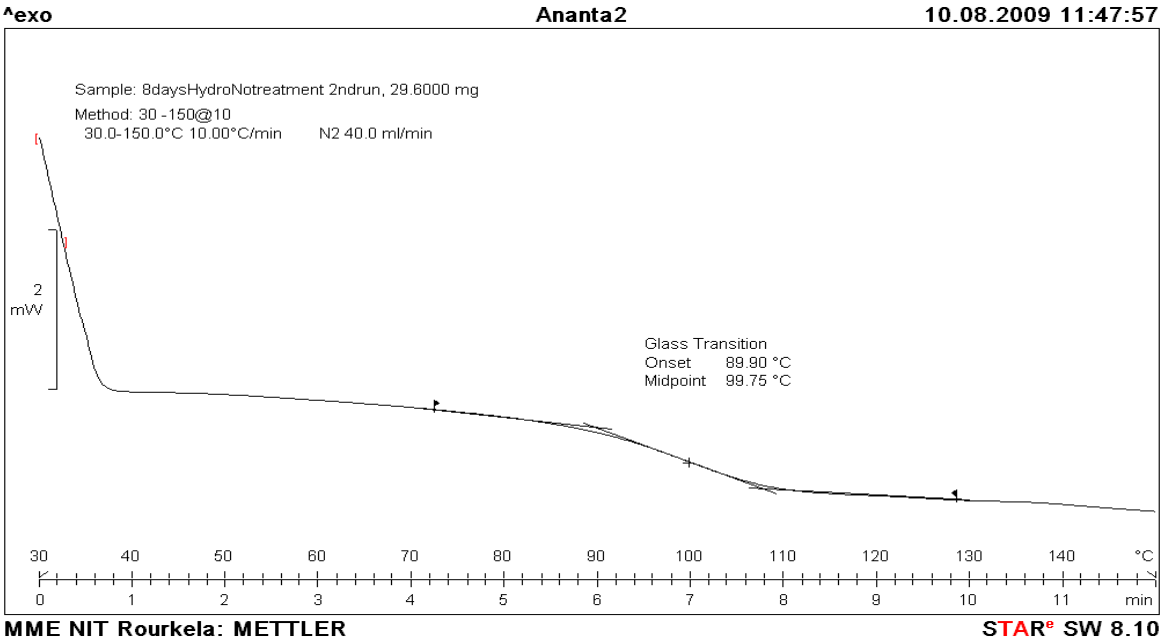

Fig: 4.26 (Glass transition temperature for 8 days hydrothermally treated sample for no shock condition)

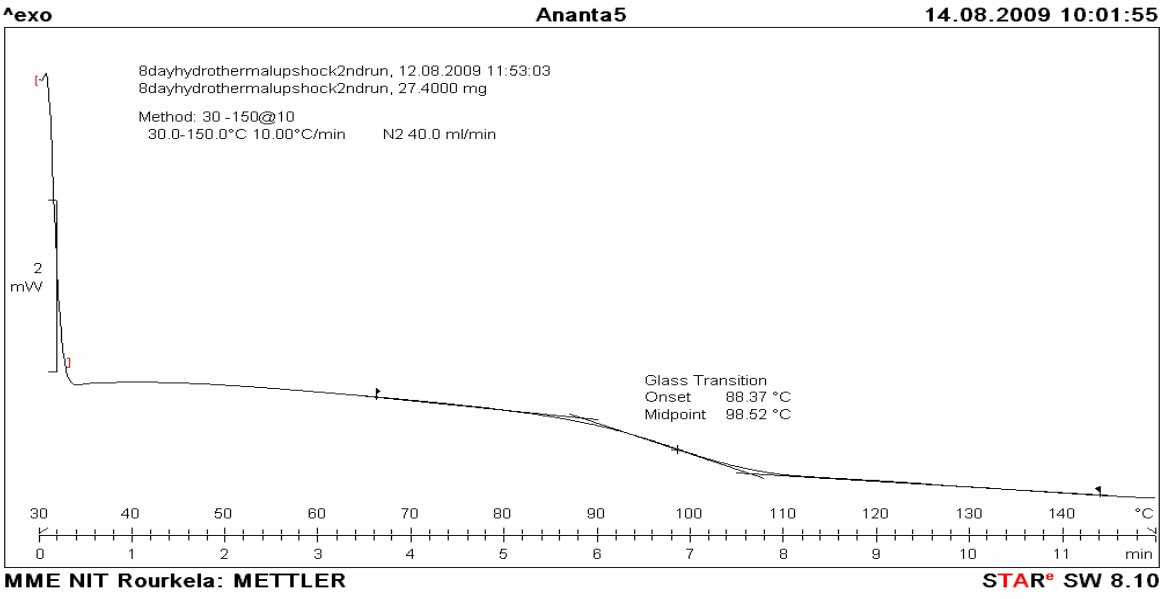

Fig: 4.27 (Glass transition temperature for 8 days hydrothermally treated sample for up–thermal shock -40^0C for 20 minutes to $+50^0$C for 30 minutes)

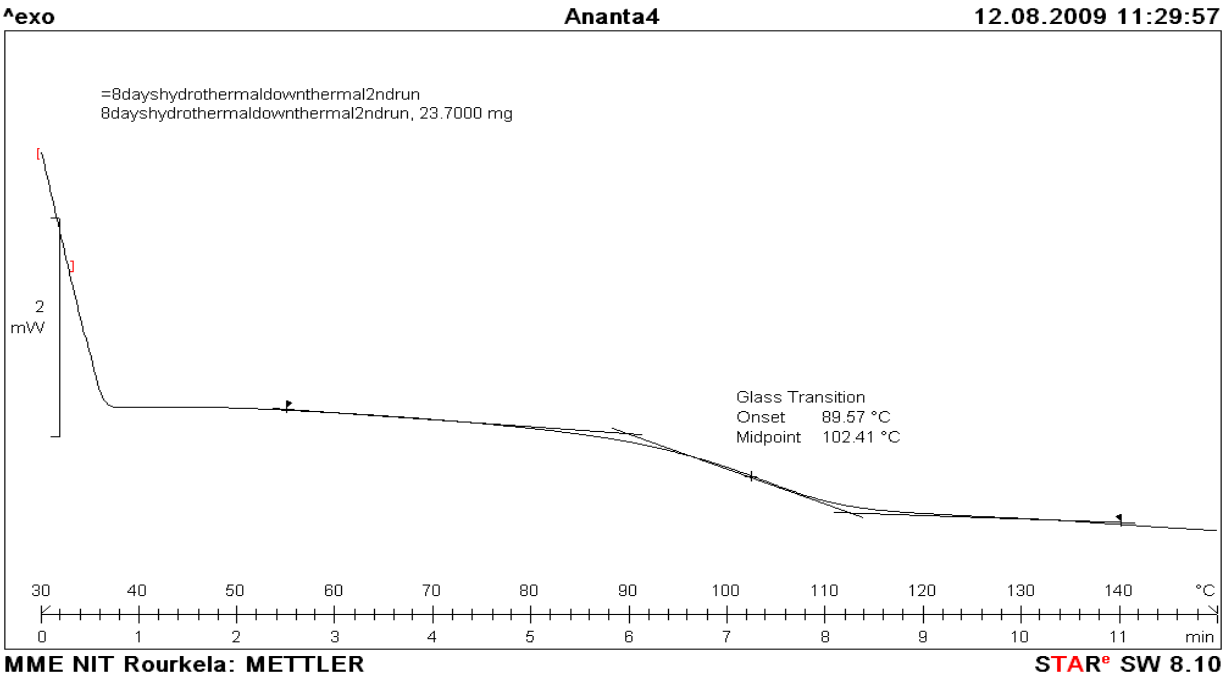

Fig: 4.28 (Glass transition temperature for 8 days hydrothermally treated sample for down–thermal shock $+50^0$C for 20 minutes to -40^0C for 30 minutes)

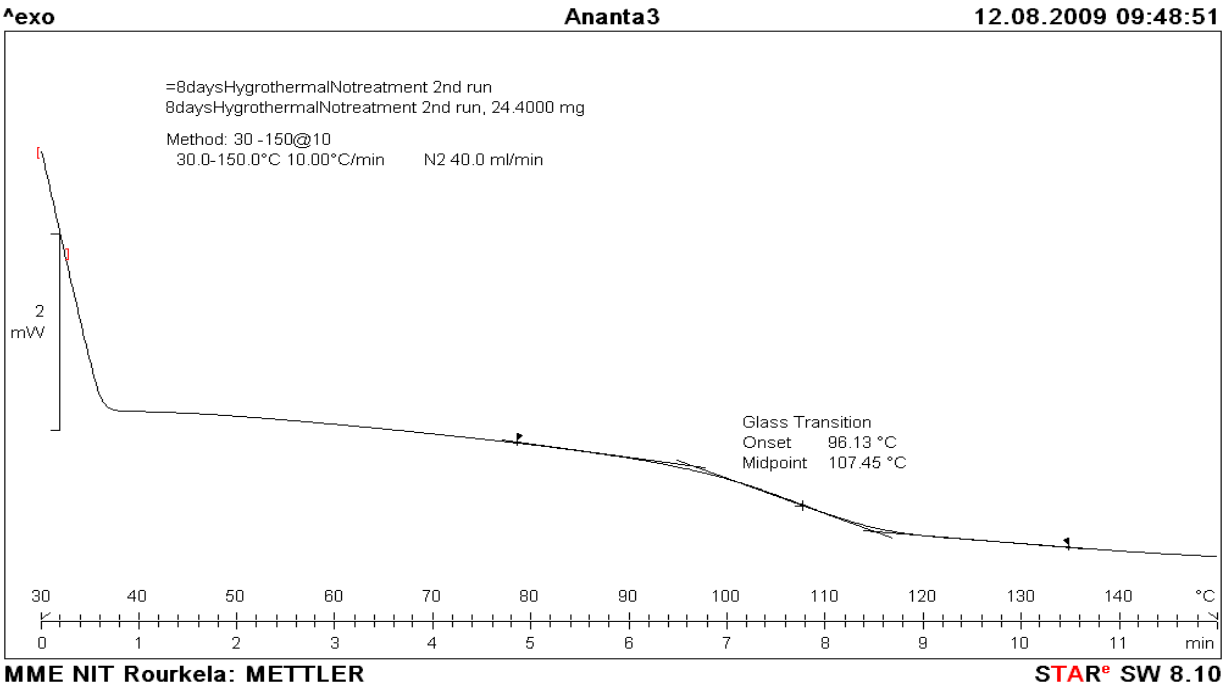

Fig: 4.29 (Glass transition temperature for 8 days hygrothermally treated sample for no shock condition)

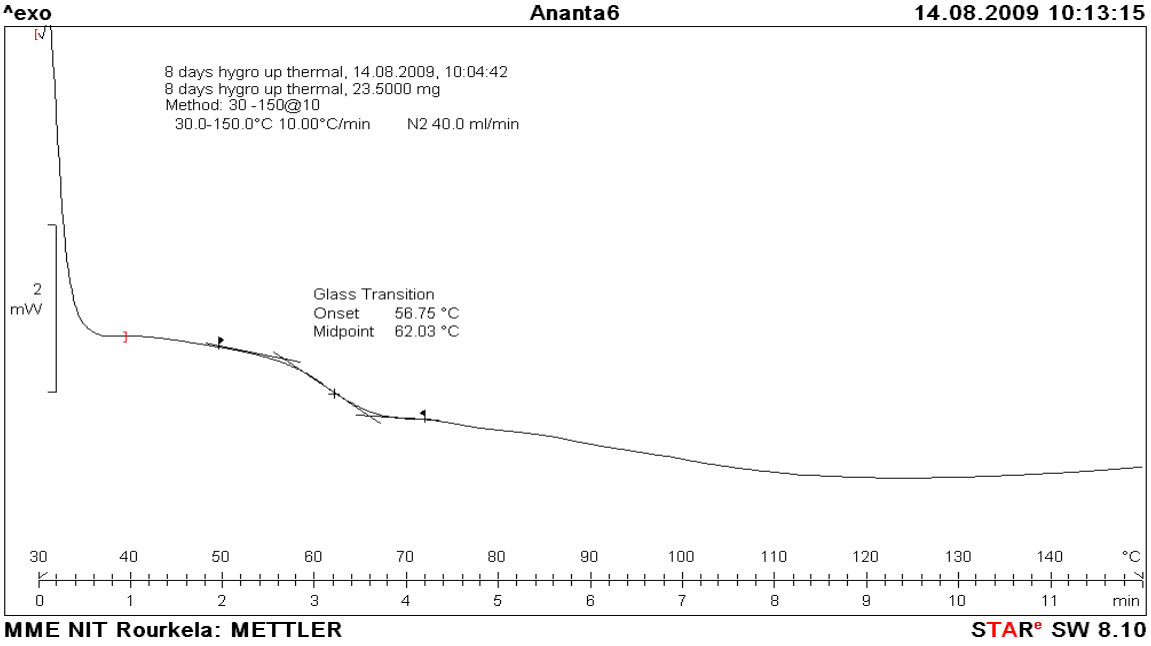

Fig: 4.30 (Glass transition temperature for 8 days hygrothermally treated sample for up–thermal shock -40^{0}C for 20 minutes to +50^{0}C for 30 minutes)

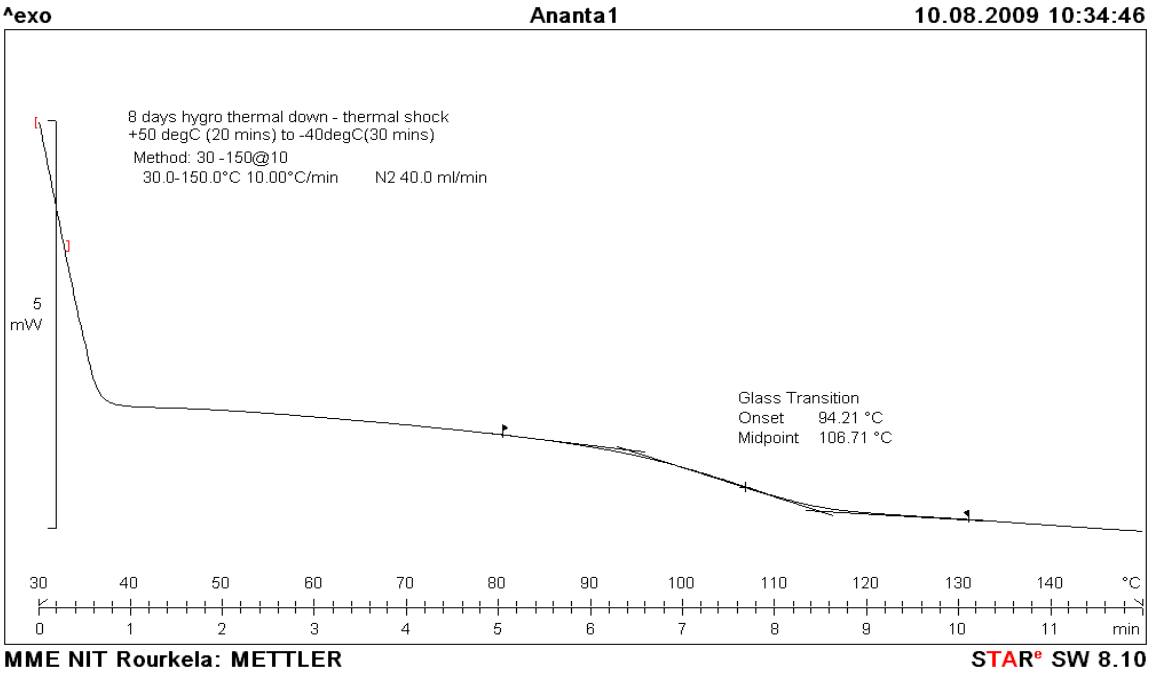

Fig: 4.31 (Glass transition temperature for 8 days hygrothermally treated sample for down–thermal shock +50^{0}C for 20 minutes to -40^{0}C for 30 minutes)

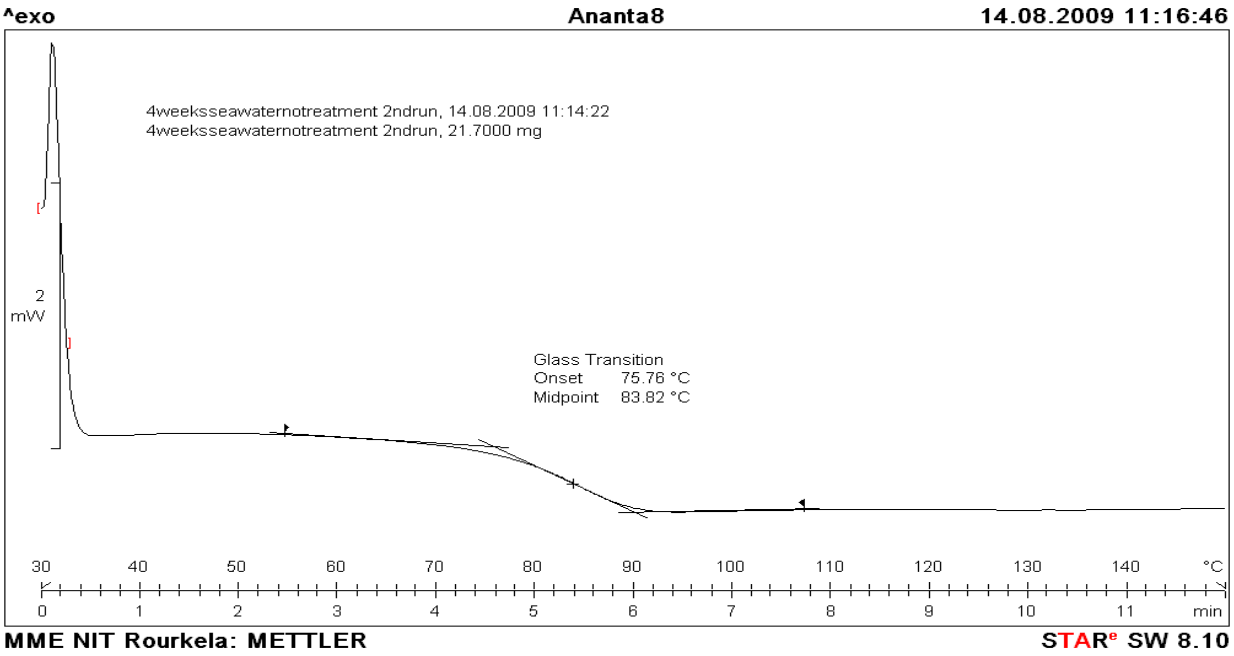

Fig: 4.32 (Glass transition temperature for 4 weeks sea water treated sample for no shock condition)

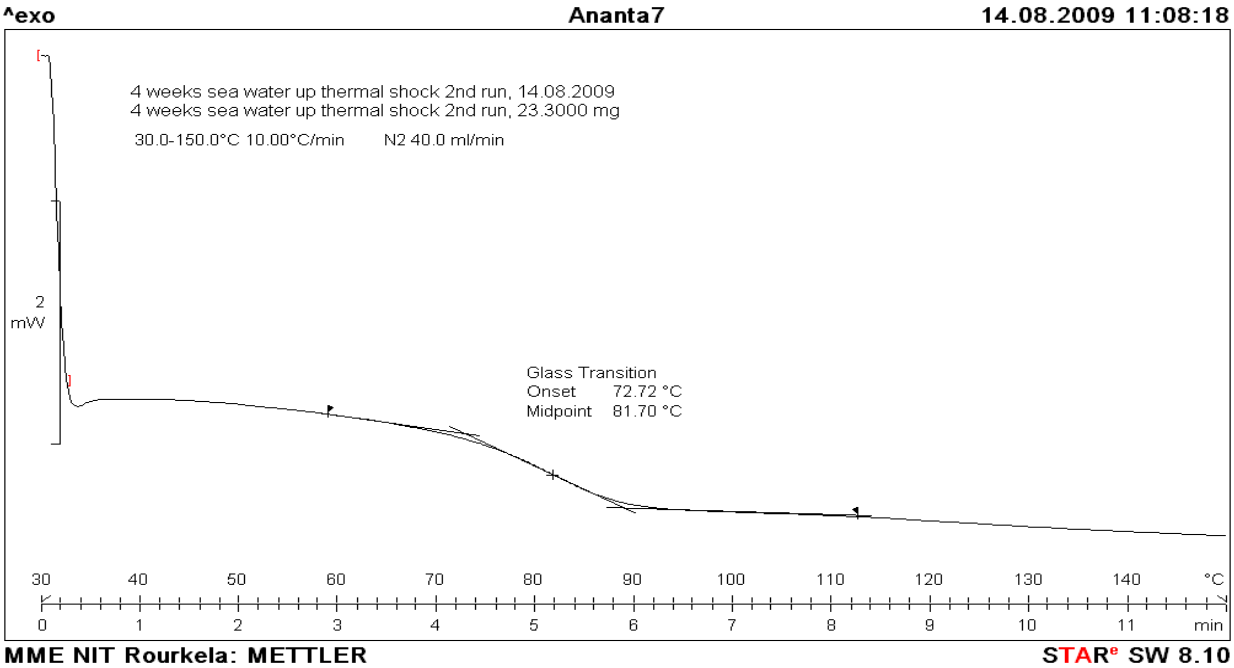

Fig: 4.33 (Glass transition temperature for 4 weeks sea water treated sample for up-thermal shock -40^{0}C for 20 minutes to +50^{0}C for 30 minutes)

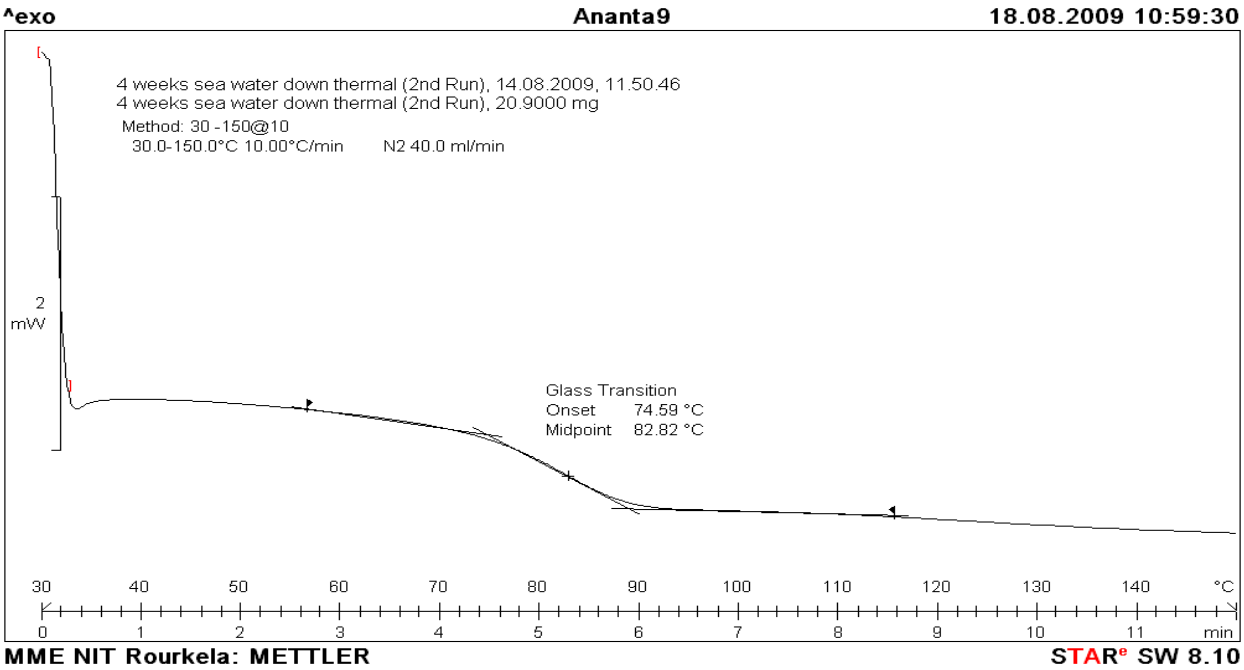

Fig: 4.34 (Glass transition temperature for 4 weeks sea water treated sample for down-thermal shock $+50^0$C for 20 minutes to -40^0C for 30 minutes)

The data reveals the following

(i) The glass transition temperature (T_g) for 8 days exposure to hydrothermal conditions and 4 weeks sea water treated sample approximately remain constant for all shock condition including no shock treatment with a very little variation.

(ii) With no thermal shock treatment the T_g for 4 weeks sea water treated sample shows the least value compared to hydrothermal and hygrothermal moisture treatment.

(iii) In the case of the sample with 8 days hygrothermal treatment the difference in the T_g value with up-thermal shock is reduced to show the greatest depression when compared to that with the sample under the same treatment with no thermal shock.

(iv) A very low value of T_g is recorded in case of the sample with 8 days hygrothermal treatment when exposed to up-thermal shock conditions.

The analysis of the findings is presented below:

The T_g (both onset and midpoint) for 8 days hydrothermal exposure and 4 weeks sea water exposure for up-thermal shock as well as down-thermal shock conditions and no shock condition do not show any considerable variations. This may be due to a similar impact on the samples due to moisture absorption and the subsequent thermal shocks. T_g is lowered when the availability of free volume is more. It is an acceptable theory that at and below the glass transition temperature $1/40^{th}$ of the total volume of the material is free volume [23]. The invariance of T_g for the cases presented above may, therefore, be due to small or no change of free volume resulting from moisture absorption followed by the thermal shock conditions.

The invariance of T_g may also have been caused due to plasticization of the matrix, which tends to lower the T_g and a simultaneous formation of hydrogen double bonds which tends to elevate the T_g as a consequence of moisture absorption [55]. We note that there is a small change in ILSS value for samples with 8 days hydrothermal exposure with no thermal shock and maximum duration of both up and down thermal shock conditions. This may be due to the fact that effect of the causes of failure such as debonding, delamination, chain swelling, etc. during the thermal shock period are not very different from that during only moisture absorption and no thermal shock under hydrothermal exposure. This may be accepted as an illustration to explain why the T_g value for 8 days hydrothermal treatment and no thermal shock is more or less maintained for the same treatment for the maximum duration of up and down thermal shock.

In case of sea water immersion for 4 weeks, though glass transition temperature (T_g) approximately remains constant, there is actually a very little depression of T_g from no shock to up-thermal as well as to down–thermal shock condition as shown in Fig: 4.25. This small depression in T_g as compared to no shock condition is prominent in case of up-thermal shock than that to down-thermal shock. This result may be attributed to the creation of more free volume with the application of up–thermal shock treatment to 4 weeks sea water treated sample. This happens due to irreversible effects caused by an up-thermal shock, which is attributed to the chemical degradation of the matrix and attack on the fiber/matrix interface. This causes the increase of internal voids of the entangling polymer chain, promoting chain

expansion and the micro cracks formation in the polymer matrix [59, 60]. Again here higher percentage of moisture absorption during sea water immersion for 4 weeks may promote the creation of more swelling stress during up-thermal shock by which the free volume generation is effective than that of down-thermal shock treatment. During down-thermal shock for maximum duration the swelling stress due to initial phase ($+50^0$C) may get dominated by the higher cryogenic compressive stress due to the later phase i.e. (-40^0C). Hence the depression of T_g for 4 weeks sea water treated sample is prominent in case of up-thermal shock treatment.

Again, the T_g for 4 weeks sea water treated sample shows the least value compared to hydro and hygroscopic moisture treatment, notwithstanding the fact that, in this case the moisture exposing time is much more than that in the other two (8 days). This implies that the larger exposing time of sea water might have generated more free volume within the epoxy network. This could have happened due to less confinement of epoxy network in a particular volume. Probably the bulky nature of various salts present in sea water with their osmotic effect [56] for a long period (4 weeks) may promote the epoxy chain extension by which the polymer network breaks up to certain extent. Hence the free volume availability will be more. This might have caused greater depression of T_g in case of 4 weeks sea water immersion than that of hydro and hygrothermal treatment. This may be due to increase of molecular mobility of the epoxide molecules by moisture ingression.

The similar behavior of T_g for 8 days hygrothermally treated sample is observed as that of 8 days hydrothermally and 4 weeks sea water treated sample. The T_g variation between no shock and down–thermal shock is very less as observed in other two moisture treated sample. This result may be attributed to the creation of less internal voids entangling the polymer chain due to down–thermal shock. During the final phase of down-thermal shock, the polymer gets rigid by the generation of cryogenic compressive stress due to -40^0C [23]. At low temperatures the polymer matrices become brittle and do not allow relaxation of residual stress or stress concentration to take place for which the chain movement is restricted which may be the cause of less depression of T_g from no shock to down-thermal shock for hygrothermally treated sample [58].

A peculiarity in the behavior of T_g for 8 days hygroscopically treated sample is observed. The rapid fall of T_g from no shock to up-thermal shock is clearly noticeable as shown in Fig: 4.24 and 4.25. This result may be attributed to the creation of more swelling stress due to $+50^0$C for (30 minutes) during the final phase of up-thermal shock [39]. For the maximum duration of up-thermal shock, some fractions of the absorbed moisture during hygrothermal treatment desorbed during final phase of the shock i.e. $+50^0$C, which might be responsible for the generation of some porosity inside the composite. During -40^0C to $+50^0$C exposing for maximum duration, the large hygro-elastic swelling stress [37] might have caused the breaking of polymer chain for which the polymer becomes more flexible by lowering the T_g which affects on mechanical properties. The desorbed moisture during the final phase of the up-thermal shock may cause some plasticizing effect by showing the early glass transition [30]. As the 8 days hygrothermally treated sample absorbed more moisture (as reported previously), the greater depression of T_g during up-thermal shock is noticeable for this sample.

4.6 SCANNING ELECTRON MICROGRAPHS

Figure: 4.35, 4.36 and 4.37 represent the scanning electron micrographs of 8 days hydrothermally treated sample for no shock, up-thermal shock and down-thermal shock condition respectively. Figure: 4.38, 4.39 and 4.40 represent the scanning electron micrographs of 8 days hygrothermally treated sample for no shock, up-thermal shock and down-thermal shock condition respectively. Figure: 4.41, 4.42 and 4.43 represent the scanning electron micrographs of 4 weeks sea water treated sample for no shock, up-thermal shock and down-thermal shock condition respectively.

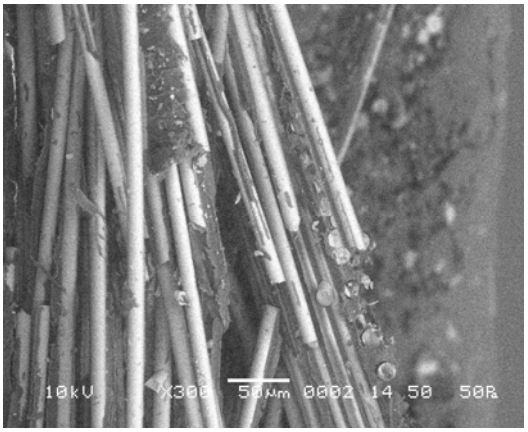

Fig: 4.35 (8 days hydrothermally treated sample without thermal shock)

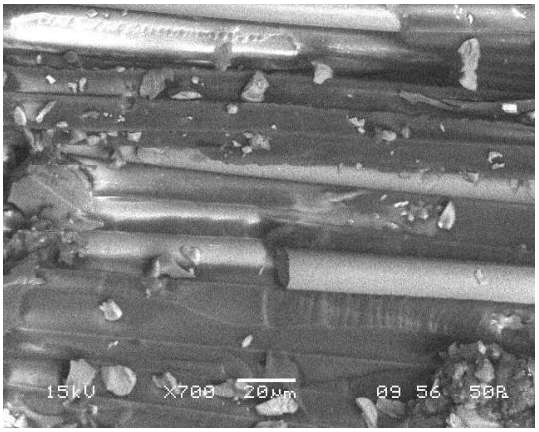

Fig: 4.36 (8 days hydrothermally treated sample after up-thermal shock)

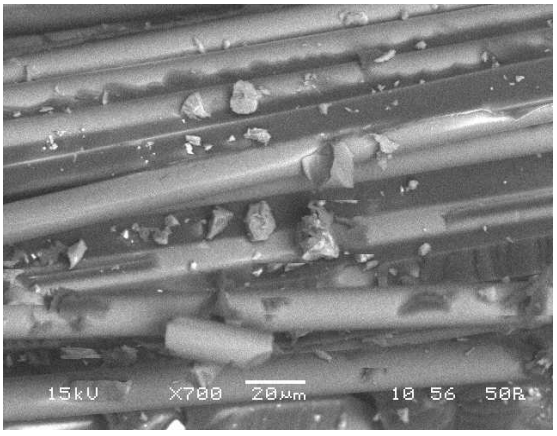

Fig: 4.37 (8 days hydrothermally treated sample after down-thermal shock)

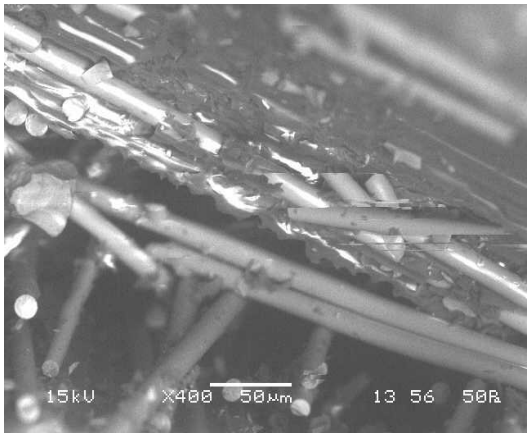

Fig: 4.38 (8 days hygrothermally treated sample without thermal shock)

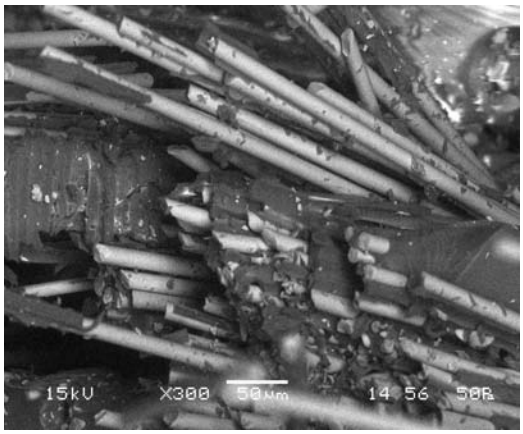

Fig: 4.39 (8 days hygrothermally treated samples after up-thermal shock)

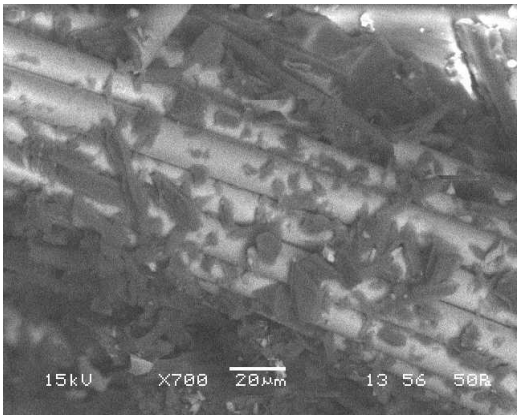

Fig: 4.40 (8 days hygrothermally treated sample after down-thermal shock)

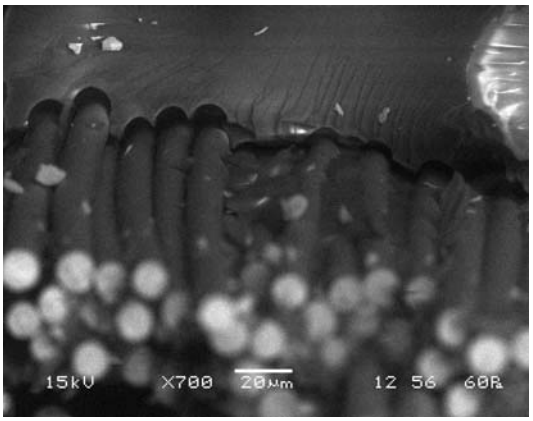

Fig: 4.41 (4 weeks sea water treated sample without thermal shock)

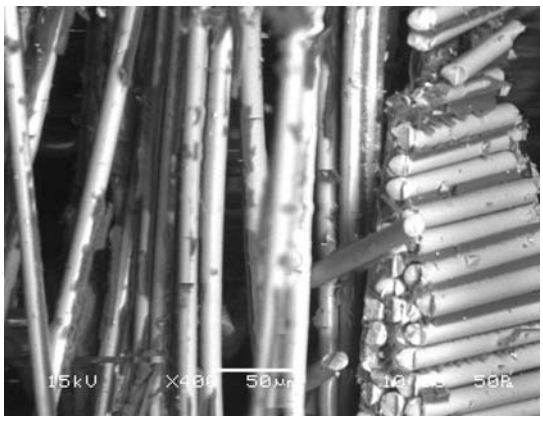

Fig: 4.42 (4 weeks sea water treated sample after up-thermal shock)

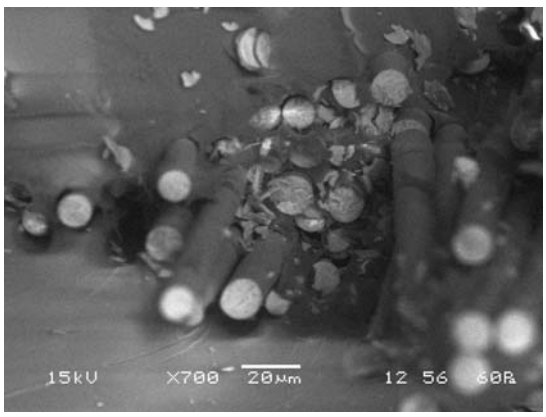

Fig: 4.43(4 weeks sea water treated sample after down-thermal shock)

From the figure: 4.35, it is evident that after immersion in distilled water for 8 days at a temperature of 65^0C, the glass fiber got detached from the epoxy matrix. The fiber/matrix adhesion hampered by this treatment which is clearly visible in this figure. The fiber fragmentation is clearly visible in figure: 4.36. This might have happened due to the generation of swelling stress in the epoxy resin with the maximum duration of up-thermal shock. The fiber breakage is also visible in figure: 4.37 which testifies for the brittle mode of failure in this sample after down-thermal shock. This might have happened due to generation of cryogenic compressive stresses during the maximum duration of down-thermal shock.

Figure: 4.38 clearly indicates the fiber breakage and fiber/matrix delamination. The plasticizing effect due to the prolonged hygrothermal treatment in huge humid atmosphere (95% R.H.) might have promoted this failure mode. Figure: 4.39 clearly indicates the matrix with signs of fiber pull out. For the samples with maximum duration of up-thermal shock after 8 days hygrothermal exposure, moisture induced swelling during moisture desorption process might have been responsible for the fiber pull out mode of failure. Figure: 4.40 represents the loosening of contact between fiber and polymer. This might have occurred due to the debonding at the interface with the application of down-thermal shock to glass fiber/epoxy composite. This resulting decrease in the corresponding ILSS value has seen in figure: 4.20 and 4.21, while analyzing the effect of exposure to the ambience with subsequent exposure to thermal shocks.

The scanning electron micrograph for 4 weeks sea water treated sample without application of thermal shock clearly indicates the fiber/matrix delamination which is shown in figure: 4.41. The prolonged exposure of glass fiber/epoxy composite to sea water for 4 weeks might have promoted the segmentations of epoxy chain by breaking of organic bonds. Hence large amount of swelling stresses could have been generated which is responsible for the interfacial delamination. The weak adhesion between glass fiber and epoxy resin after sea water immersion to 4 weeks might have been responsible for the fiber breakage during loading of the crosshead of INSTRON. The fibers have been separated from each other and have got debonded as shown in figure: 4.42. The desorption of saline water during the maximum duration of up-thermal shock might have promoted the swelling of epoxy resin

which could have caused for the loss of contact between fiber-matrix and debonding. The matrix with fiber pull out is observed from the scanning electron micrograph figure: 4.43. Due to large misfit of strain between glass fiber and epoxy resin, rapid fall of ILSS is observed for this sample during maximum duration of down-thermal shock as shown in figure: 4.22 earlier in the thesis. This may be attributed to the interfacial deadhesion and debonding between fiber and the polymer matrix. Again the generation of cryogenic compressive stresses during down-thermal shock could have increased the rigidity of the polymer as a consequence of which the fiber pull-out is observed during loading condition.

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Chapter-5

CONCLUSIONS

CONCLUSIONS

The following conclusions can be arrived at from the results of the present project work.

5.1 MOISTURE ABSORPTION:

- Moisture ingression into the composite is diffusion driven, the water molecule being transported into the matrix and in some cases into the fiber.
- Hygrothermal exposure shows greatest moisture pick up in the initial stages.
- Total moisture pick up under hydrothermal condition is less than that under hygrothermal condition for similar length of exposure time.
- Sea water immersion reveals an anomalous nature of moisture ingression, the rate of ingression being the lowest at the beginning than picking up and then again slowing down.
- In all cases of moisture ingression the weight percent moisture uptake shows a continuing uptake trend and not a plateau even after a prolonged time of exposure to the respective ambience.
- It is thus concluded that in all the cases examined longer exposures to moisture assist further moisture pick up by delaying the saturation level of moisture in the composite body.

5.2 ILSS WITH NO-THERMAL SHOCK:

- As compared to the ‘as-cured’ sample ILSS value of samples with hydrothermal exposure decreased initially while showing a considerable increase later on.
- In case of hygrothermal exposure, as compared to the ‘as-cured’ sample the ILSS decreased continuously with some minor fluctuations.
- For the sample immersed in sea water the ILSS values, after initial fluctuation nosedived to a very small value.

5.3 ILSS WITH UP-THERMAL SHOCK:

- In general, a longer exposure to up-thermal shock for hydrothermal exposure cause a convergence of the ILSS value to a narrow range of values after an initial fluctuation.
- The longest exposure to the hygrothermal condition (8-days in this case) shows a gradual decrease in ILSS value with increased duration of the up-thermal shock treatment.
- The up-thermal shock for shorter duration exhibited an increasing trend of the ILSS value for samples with hygrothermal condition while a longer duration of the thermal shock for the same samples actually reveal a decreasing trend in the ILSS value.
- For the sea water treated sample with the longest period of immersion (4 weeks in this case) the ILSS value showed an increasing trend for shorter durations of the up-thermal shock while longer duration of the same shock sample did not cause any noticeable variation in the ILSS values.

5.4 ILSS FOR DOWN-THERMAL SHOCK:

- For longer duration of down-thermal shock the ILSS values of hydrothermally treated samples converge to some range of values.
- After initial decreasing trend all the hygrothermally treated samples show a fluctuating trend in the ILSS values at longer duration of the down-thermal shock.
- For sea water immersion for the longest period an exposure to down-thermal shock for the maximum duration (30 minutes in this case) the ILSS is seen to fall down to very low value.

5.5 VARIATION OF GLASS TRANSITION TEMPERATURE (T_g)

- Both up-thermal shock and down-thermal shock do not affect the T_g much as compared to the value under no-shock condition for samples with sea water as well as hydrothermal exposure.
- The lowest value of T_g is recorded for the 8-days hygrothermally treated sample under up-thermal shock.
- Variation of T_g under the same hygrothermal exposure is negligible for down-thermal shock as compared to the no-thermal shock condition.

5.6 FAILURE MODES:

- The SEM micrographs establish fiber-fragmentation, fiber pull-out, fiber-matrix debonding, delamination, etc to be the chief mode of failure.

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Chapter-6

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REFERENCES

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